PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
P22231/GST/RMC		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/GB 99/ 02482	29/07/1999	29/07/1998

Applicant

THE COURT OF NAPIER UNIVERSITY et al.

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form

[ ] furnished subsequently to this Authority in computer readble form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

[ ] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/02482

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G02B1/04 F21V8/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G02B F21V

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5 579 429 A (NAUM DANIEL) 26 November 1996 (1996-11-26) claims 1-15 column 7, line 32 -column 8, line 44 column 15, line 36 -column 18, line 14 ---	1-14
X	WO 93 05365 A (WELMED LTD ;COVENTRY UNIVERSITY ENTERPRISE (GB)) 18 March 1993 (1993-03-18) claims 1-12 page 2, line 6 -page 3, line 2 page 3, line 31 -page 4, line 24 --- -/--	1

[X] Further documents are listed in the continuation of box C

[X] Patent family members are listed in annex.

Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 November 1999	26/11/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Depijper, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

[redacted]national Application No
PCT/GB 99/02482

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 187 561 A (COMMISSARIAT ENERGIE ATOMIQUE) 16 July 1986 (1986-07-16) claims 1-18 page 4, column 6, line 47 - line 64 page 5, column 7, line 1 -page 6, column 9, line 16 page 6, column 9, line 43 - line 46	1,7
X	FR 2 588 972 A (GREMILLET DOMINIQUE) 24 April 1987 (1987-04-24) claims 1-10 page 1, line 8 - line 30 page 2, line 5 - line 33	1-3,7,8
X	WO 90 07766 A (HUGHES AIRCRAFT CO) 12 July 1990 (1990-07-12) claims 1-49 page 6, line 6 -page 7, line 15 page 10, line 24 -page 12, line 35; figure 3	1,7
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 399 (P-651), 26 December 1987 (1987-12-26) & JP 62 161105 A (SHARP CORP), 17 July 1987 (1987-07-17) abstract	1
A	US 4 425 907 A (YOUNGHOUSE LAWRENCE B) 17 January 1984 (1984-01-17) claims 1,4 column 2, line 17 - line 41 column 2, line 58 -column 3, line 37	1
A	EP 0 539 615 A (DAITO SANGYO CO LTD ;NIPPO CO LTD (JP)) 5 May 1993 (1993-05-05) claims 1-12 page 3, column 3, line 23 -column 4, line 36 page 4, column 6, line 21 - line 38	1,7,8

1

INTERNATIONAL SEARCH REPORT

[redacted]mation on patent family members

[redacted]national Application No
PCT/GB 99/02482

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5579429 A	26-11-1996	NONE	
WO 9305365 A	18-03-1993	EP 0623208 A	09-11-1994
		US 5561732 A	01-10-1996
EP 0187561 A	16-07-1986	FR 2574564 A	13-06-1986
		US 4812013 A	14-03-1989
		US 4753512 A	28-06-1988
FR 2588972 A	24-04-1987	NONE	
WO 9007766 A	12-07-1990	US 4989956 A	05-02-1991
		CA 2006050 A,C	04-07-1990
		DE 68918586 D	03-11-1994
		DE 68918586 T	26-01-1995
		EP 0402458 A	19-12-1990
		JP 3503094 T	11-07-1991
		MX 171589 B	08-11-1993
JP 62161105 A	17-07-1987	NONE	
US 4425907 A	17-01-1984	NONE	
EP 0539615 A	05-05-1993	NONE	

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 15 March 2000 (15.03.00)	
International application No. PCT/GB99/02482	**Applicant's or agent's file reference** P22231/GST/RMC
International filing date (day/month/year) 29 July 1999 (29.07.99)	**Priority date** (day/month/year) 29 July 1998 (29.07.98)
Applicant HAJTO, Janos et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

17 February 2000 (17.02.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Juan Cruz
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

Form PCT/IB/331 (July 1992)

3163694

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P22231/GST/RMC	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB99/02482	International filing date *(day/month/year)* 29/07/1999	Priority date *(day/month/year)* 29/07/1998
International Patent Classification (IPC) or national classification and IPC G02B1/04		
Applicant THE COURT OF NAPIER UNIVERSITY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 17/02/2000	Date of completion of this report 16.08.00
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Thieme, W Telephone No +49 89 2399 2597

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02482

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-27 as originally filed

Claims, No.:

1-16 as received on 31/07/2000 with letter of 28/07/2000

Drawings, sheets:

1/29-29/29 as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1,2,4,5,6,10
Inventive step (IS)	Yes:	Claims	
	No:	Claims	3,7,8,9,11-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The subject matter of claim 1 is not novel within the meaning of Art.33 PCT.

1.1 Document D1 (US, 5 579 429, A) discloses the use of a fluorescent dye doped polymer as an optical fibre in a visual display (see for example figures 20A and 20B: fibre portions 204 forming the term "EXIT"). Fluorescent light is generated when artificial ambient light enters the doped polymer material (see light source 206 disposed to pump optical fibres 204). The optically transparent polymer is doped with organic fluorescent dye molecules such as Coumarin 314 (see page 7, line 56).

Thus, claim 1 does not satisfy the criteria set forth in Art.33 PCT as to novelty, since for each feature a counterpart can be found in document D1.

2. The display of claim 5 is not novel either.

2.1 Document D1 (US, 5 579 429, A) discloses a display including a plurality of fibres which comprise a dye doped polymer as defined in claim 1 (see section 1.1 above). In addition to that, document D1 teaches the reader the use of a mixture of dyes (see column 15, lines 27 to 32).

Thus, claim 5 does not satisfy the criteria set forth in Art.33 PCT as to novelty, since for each feature a counterpart can be found in document D1.

3. The dependent claims do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being as follows:

Claim 2:
The materials are known from document D1 (see column 6, line 21 to 67)

Claim 3:
The dimensions are typical for optical fibre displays of the type presented in figures 20 of document D1

Claim 4:
The formula appears also to be applicable to the fibres of the display presented in figures 20 of document D1

Claims 6 to 9:
The use of two or three dyes is obvious in view of the suggested use of a mixture of dyes

Claim 10:
Figures 20 of document D1 disclose a display composed of a plurality of fibres

Claims 11 to 16:
The provision of reflectors performing the role of total internal reflection is known from figure 21C of document D1; the provision of a reflection coating on a light guiding polymer panel is suggested at page 9, last paragraph of document D2 (WO, 93 05365, A). The use of dielectric layers as well as polymer layers of differing index is state of the art.

Claims

1. A fluorescent dye doped polymer for use as an optical fibre, a film or sheet wherein an optically transparent polymer is doped or blended with organic fluorescent dye molecules for use in visual display wherein fluorescent light is generated when artificial ambient light, daylight or sunlight enters the doped polymer or optical fibres.

2. A fluorescent dye doped polymer, as claimed in Claim 1, wherein the transparent polymer is chosen from the group comprising PMMA, polycarbonate and polystyrene.

3. A fluorescent dye doped polymer, as claimed in Claim 1, wherein any organic fluorescent dye is used.

4. A fluorescent dye doped polymer, as claimed in Claim 1, wherein the fluorescent dye molecules are chosen from a group comprising: PBD, Bis-MSB, 3-3'-diethyloxycarbocyanine-iodide and cresyl violet 670 perchlorate.

5. A fluorescent dye doped polymer, as claimed in Claim 1, where the polymer forms an optical fibre, the radius of such a fibre is between 0.25 and 0.70 x 10^{-2} meters and the length of the fibre is between 0.2 and 1.6 meters.

6. An fluorescent dye doped polymer claimed in Claim 5 wherein the magnitude of the fluorescent light emitted from such a fibre is given by the equation $Aa/Ae = 2L/r$ wherein Aa is the surface area of the fibre and Ae is the area at which the fluorescent light is emitted.

7. A fluorescent dye doped polymer, as claimed any of Claims 1 to 6, for use as a display pixel, where artificial ambient light or sunlight provides excitation sources.

8. A display comprising a fluorescent dye doped polymer, as claimed in any of the preceding claims, consisting of a plurality of fibres, which may include individual fibres which emit an alternative, predetermined colour of light, whereby the light is defined by the fluorescent dye which is doped within the polymer.

9. A display as claimed in Claim 8, in a flat panel conformation wherein the bottom surfaces and edges of the polymer film are covered with a highly reflective additional layer which acts as a mirror performing the role of total internal reflection of all light entering into the polymer.

10. A flat panel display as claimed in Claim 9, whereby the top surface of the polymer is covered with a dielectric stack mirror.

11. A flat panel display as claimed in Claim 9 or 10, wherein the stack is constituted of an alternating sequence of two dielectric films with alternately high and low refractive indices.

12. A flat panel display as claimed in Claim 10, comprising a dielectric stack whereby the composition of this dielectric stack acts as an interference filter to allow substantially 100% transmission of light from air into the polymer for wavelengths used for excitation of the dye.

13. A flat panel display as claimed in any of Claims 9 to 11, where the stack has substantially 100% reflection for light wavelengths emitted from the fluorescent dyes, the dielectric layers have been vacuum evaporated, spin coated or sputtered onto the surface of the polymer.

14. A display as claimed in Claim 12 , whereby thin films of two different polymers, with the two different refractive indices, can be applied to the

polymer surface sequentially and vacuum pressed and/or thermally treated for each layer.

Claims

1. Use of a fluorescent dye doped polymer as an optical fibre, a film or a sheet in a visual display, in which fluorescent light is generated when artificial ambient light, daylight or sunlight enters the doped polymer or optical fibres, characterised in that the optically transparent polymer is doped or blended with organic fluorescent dye molecules chosen from a group comprising PBD, Bis-MSB, 3-3'-diethyloxycarbocyanine-iodide, cresyl violet 670 perchlorate, coumarin 6, coumarin 7, coumarin 314, 1,8-Diphenyl-1,3,5,7,-octatetrene, Nile red, Sulforhodamine 101 and Solforhodamine 640.

2. Use of a polymer as claimed in Claim 1 wherein the transparent polymer is chosen from the group comprising PMMA, polycarbonate and polystyrene.

3. Use of a polymer as claimed in Claim 1 wherein the polymer is an optical fibre, the radius of which is between 0.25 and 0.70 x 10^{-2} meters and the length of the fibre is between 0.2 and 1.6 meters.

4. Use of a polymer as claimed in Claim 3 wherein the magnitude of the fluorescent light emitted from such a fibre is given by the equation Aa/Ae=2L/r wherein Aa is the surface area of the

fibre and Ae is the area at which the fluorescent light is emitted.

5. A display comprising a fluorescent dye doped polymer as defined in any of the preceding claims, consisting of a plurality of fibres which may include individual fibres, a film or a sheet, which polymer when excited by light emits the characteristic colour of the dye, characterised in that the polymer is doped with a combination of dyes.

6. A display as claimed in Claim 5 wherein the polymer is doped with two or three dyes

7. A display as claimed in Claim 6 wherein the polymer is doped with Nile Red and Coumarin 6.

8. A display as claimed in Claim 6 wherein the polymer is doped with Nile Red 0.04% and Coumarin 6.

9. A display as claimed in Claim 6 wherein the polymer is doped with Nile Red 0.04%, Coumarin 6 and Bis-MSB.

10. A display as claimed in any one of Claims 5 to 9 consisting of a plurality of fibres acting as pixels.

11. A display as claimed in any one of Claims 5 to 9 in a flat panel conformation wherein the bottom surfaces and edges of the polymer film are covered with a highly reflective additional layer which acts as a mirror performing the role of total internal reflection of all light entering into the polymer.

12. A flat panel display as claimed in Claim 11 whereby the top surface of the polymer is covered with a dielectric polymer film.

13. A flat panel display as claimed in Claim 11 or Claim 12 wherein the stack is constituted of an alternating sequence of two dielectric films with alternately high and low refractive indices.

14. A flat panel display as claimed in Claim 12 comprising a dielectric stack whereby the composition of this dielectric stack acts as an interference filter to allow substantially 100% transmission of light from air into the polymer for wavelengths used for excitation of the dye.

15. A flat panel display as claimed in any one of Claims 11 to 13 where the stack has substantially 100% refection for light wavelengths emitted from the fluorescent dyes, the dielectric layers have been vacuum

evaporated, spin coated or sputtered onto the surface of the polymer.

16. A display as claimed in Claim 14 whereby thin films of two different polymers, with the two different refractive indices, can be applied to the polymer surface sequentially and vacuum pressed and/or thermally treated for each layer.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : G02B 1/04, F21V 8/00

A1

(11) International Publication Number: **WO 00/07039**

(43) International Publication Date: 10 February 2000 (10.02.00)

(21) International Application Number: PCT/GB99/02482

(22) International Filing Date: 29 July 1999 (29.07.99)

(30) Priority Data:

9816490.8	29 July 1998 (29.07.98)	GB
9820064.5	16 September 1998 (16.09.98)	GB

(71) Applicant *(for all designated States except US)*: THE COURT OF NAPIER UNIVERSITY [GB/GB]; 10 Colinton Road, Edinburgh EH10 5DT (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: HAJTO, Janos [GB/GB]; 36 Liberton Gardens, Edinburgh EH16 6JS (GB). HINDLE, Colin [GB/GB]; 9 Glengyle Terrace, Edinburgh EH9 9LU (GB). GRAHAM, Andrew [GB/GB]; 11 Bailie Terrace, Edinburgh EH15 3BT (GB).

(74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: DISPLAYS

(57) Abstract

The present invention describes a fluorescent dye doped polymer based optical wave–guide structure. The described polymers can be used to fabricate a range of display elements and illumination systems which work without the use of external electrical power. This is due to the process of the fluorescent dyes absorbing ambient light and then subsequently emitting light which is conducted by the polymer host material to a point where it is emitted. The emitted light can be of a range of colours depending upon the type of dye that polymers are doped with. There is a constant contrast between the light power flux emitted for the wave–guide structure and the light power flux of the ambient light. There is also provided a method in which a dielectric stack mirror layer fabricated on the surface of the polymer which can be used to improve the efficiency and the contrast of those optical elements.

FOR THE PURPOSES OF INFORMATION ONLY

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DISPLAYS

This invention relates to display and illumination technology.

The present invention describes a method in which polymers doped with fluorescent dyes can be used to fabricate display elements and illumination systems for use in applications such as road signs, advertisement displays, toys etc whereby the use of external electrical power is not required. The fluorescent dyes with which these polymers are doped, absorb ambient light, before emitting light which is conducted by the polymer host material to the end of the fibre where the emitted light is of a much greater light power density than the light power density of the ambient light.

In this field it is already known that flat panel display elements composed out of plastic polymers can be used as display articles and that optical fibres can be used to convey information in telecommunication or in display technology.

Previous application involving such materials had the disadvantage that the sign or display element required illumination through the means of applying an external

electrical power supply with this electrical power requiring conversion into light power and consequently this method consumes electrical power. Similarly, in the case of optical fibres, a light source had to be located at one end of the fibre to allow transmission and emission of light at the other end of the fibre.

The optical power density from the fluorescent polymer is higher than the optical power of the ambient light. The ratio between these optical power densities does not depend on the ambient light conditions as long as they are sufficient for excitation of the fluorescent dye.

The suggested new technology does not require any external electrical power because it is extracting light power directly from ambient light (sunlight or artificial light).

The suggested new technology is inherently safer compared to conventional electrical power based technologies it does not use any external or internal voltages and/or currents for its operation.

Another advantage of using the suggested new technology is associated with the fact that it does not require maintenance since it does not use electrical cables.

Further advantages include the technology used in this invention being simple, environmentally friendly, having a one hundred percent recycling capacity and not using the Earth's resources.

Fluorescent dye doped polymers are used to collect ambient light through the introduction of red, green and blue light emitting fluorescent dyes into a polymer host material. The colour of the emitted light can be changed into a required specification through variation of the dyes incorporated into the polymer.

In the case of the polymer taking the form of an optical fibre, through a suitable

combination of optical fibre geometry and (length and diameter) and the incorporation of an appropriate fluorescent dye, the light power density at the end of the fibre (light emitter) can be made much larger than the light power density of the ambient light and therefore can be used for illumination or display applications. Furthermore, the contrast between the light power density at the end of the fibre and the light power density of the ambient light remains constant because this parameter only depends on the geometrical and material parameters for a given polymer, but does not depend on the ambient light conditions. The end of the fibres can be used as light emitting pixels in an array. By modulating the light intensity at the end of each fibre selectively, the fibre array can be used as a display device.

The principle of operation is shown in Figure 1 wherein an optical fibre polymer is shown to be doped with fluorescent dye molecules. Similarly, a transparent polymer film or sheet could also be chemically doped or blended with a fluorescent dye. The fluorescent dye should have a high quantum efficiency for converting natural light or indoor light into some visible colour.

It is an object of this present invention to provide a transparent polymer which can be formed into a film, a sheet, an optical fibre, or similar for use in illumination and display applications.

According to the present invention there is provided an optically transparent polymer, such as an optical fibre, a film or sheet which is doped or blended with organic fluorescent dye molecules for use in visual display wherein fluorescent light is generated when artificial ambient light, daylight or sunlight enters the doped polymer or optical fibres.

Whereas in general any transparent polymer may be used, suitably the transparent polymer is chosen from the group comprising PMMA, polycarbonate and polystyrene.

Whereas in general any organic fluorescent dye can be used, suitably the fluorescent dye molecules are chosen from the group comprising PBD, Bis-MSB, 3-3'-diethyloxycarbocyanine-iodide and cresyl violet 670 perchlorate.

Preferably where the polymer constitutes an optical fibre, the preferred embodiment of the radius of such a fibre is between 0.25 and 0.70 x 10^{-2} meters and the length of the fibre is between 0.2 and 1.6 meters.

Where the preferred embodiment of this invention is an optical fibre , the magnitude of the fluorescent light emitted from such a fibre is given by the equation Aa/Ae = 2L/r wherein Aa is the surface area of the fibre and Ae is the area at which the fluorescent light is emitted.

Although a preferred dimension for the radius of an optical fibre embodiment is given, clearly the dimensions of the fibres will depend on their use in proposed displays.

The invention also provides the use of the fibres as display pixels where artificial ambient light or sunlight provides excitation sources.

The invention further provides display devices comprising a plurality of fibres as described herein.

The plurality of fibres may include fibres to emit a variety of colours.

The devices may further comprise shutters to control emission from the individual fibres in a device.

Preferably where there exists a flat panel display or sheet embodiment of this invention, the bottom surfaces and edges of the polymer film are covered with a

highly reflective additional layer which acts as a mirror performing the role of total internal reflection of all light entering into the polymer.

Preferably also in such embodiments, the top surface of the polymer shall be covered with a dielectric stack mirror. In a preferred embodiment of this stack it is constituted of an alternating sequence of two dielectric films with alternately high and low refractive indices.

The composition of this dielectric stack is such that the aforementioned stack shall act as an interference filter to allow nearly 100% transmission of light from air into the polymer for wavelengths used for excitation of the dye. Further this aforementioned stack has nearly 100% reflection for light wavelengths emitted from the fluorescent dyes. The dielectric layers can be vacuum evaporated, spin coated or sputtered onto the surface of the polymer.

In an alternative preferred embodiment of this dielectric stack, thin films of two different polymers, with the two different refractive indices, can be applied to the polymer surface sequentially and vacuum pressed and/or thermally treated for each layer. This method has the advantage that it allows larger areas to be covered by the dielectric stack mirror.

Alternatively, cladding can also be used for the same purpose although the efficiency is not as good as with the dielectric stack mirror.

The present invention can be adapted for display purposes as the fluorescent light emitted from the dye can be coupled out from the polymer at the top surface by emitting or removing the dielectric stack mirror at a given surface area and by making an uneven or grated surface at the polymer air interface. The grating structure should be maximised for maximum diffraction for the emitted fluorescent light wavelength.

In an alternative preferred embodiment of this form of the invention, the replacement of the bottom mirror layer of the dielectric stack mirror, identical to the one applied to the top surface allows a combined reflective and transmissive mode of light collection and display operation.

Further an alternative preferred embodiment of the invention provides a further combination of dielectric stack and mirror combinations while using the principles previously described. In this embodiment the dielectric stack mirror is applied on both sides of the transparent polymer-dye matrix but no side mirrors are applied. Consequently the fluorescent light generated inside the polymer will be waveguided towards the edges of the polymer.
The invention also provides methods for producing displays as set out herein.

The invention will now be described with reference to the accompanying figures wherein:

Figure 1 describes the principles of Fluorescent Dye Doped Optical

Figure 2 shows Absorption-Emission spectra of Nile Red in Polystyrene

Figure 3 shows Absorption-Emission spectra of Coumarin 6 in Polystyrene

Figure 4 shows Absorption-Emission spectra of BisMSB in Polystyrene

Figure 5 shows NR 0.04 wt% + C6 in Polystyrene vs. wavelength.

Figure 6 illustrates Nile Red + Coumarine 6 in Polystyrene.

Figure 7 illustrates Absorption - Emission Area of Nile Red 0.04 % + Coumarine 6 + Bis MSB.

Figure 8 illustrates Quantum Yield of Coumarin 6 in polystyrene.

Figure 9 shows Absorption - Emission Area of Coumarin 6 in Polystyrene.

Figure 10 shows Quantum Yield of Bis MSB in Polystyrene.

Figure 11 illustrates Arrangement for light scattering/Absorption measurements.

Figure 12 describes Scattered light intensity from polycarbonate red and green fibres.

Figure 13 demonstrates Polycarbonate Fibres/ Polycarbonate with red/green laser

Figure 14 demonstrates Intensity of green/red fibre in sunlight while fibres are partially covered (normalised and an average of 7 measurements/ y-errors equal 2 sigma.

Figure 15 shows Structure of Light Emitting Polymer in combined reflective and transmissive mode.

Figure 16 shows the structure of Light Emitting Polymer in the Edge emitting.

Figure 17 demonstrates Green Reflectance.

Figure 18 demonstrates GREEN1 Transmittance.

Figure 19 demonstrates RED1 Reflectance

Figure 20 demonstrates RED1 Transmittance

Figure 21 shows a display in full sunlight conditions.

Figure 22 shows a display in cloudy conditions

Figure 23 shows a display in late evening condition (two hours after sunset).

Detailed Description of Figures

Figure 1: Fluorescent Dye Doped Optical Waveguide; describes the principle of operation for the fluorescent dye doped polymer optical fibre. The principle steps of operation are as follows:

1) Ambient light is absorbed by fluorescent dye,
2) Dye re-emits fluorescent light
3) Fluorescent light is waveguided if angle of incidence $\gamma >= \theta c$ where θc = critical angle for total internal reflection
4) Fluorescent light is leaked out of the waveguide if $\gamma < \theta c$

The intensity of the fluorescent light at the end of the optical waveguide depends on the following physical parameters;

Ambient light intensity
Overlap of the spectral distribution of the ambient light and the light absorption of the fluorescent dye
Absorption coefficient of the dye in the light absorption region
Absorption coefficient of the polymer core and polymer cladding in the light absorption region
Absorption coefficient of the polymer core and polymer cladding in the fluorescent light emission region
Refractive index of the polymer core
Refractive index of the polymer cladding

Optical uniformity of the core (scattering)

Optical uniformity of the cladding (scattering)

Geometry of the optical waveguide structure

Optimisation of these parameters results in an optical power flux emitted at a selected spectrum of wavelengths from the end of the waveguide at an increased flux than the flux of the ambient light i.e. optical amplification is obtained.

Figure 2: Absorption-Emission spectra of Nile Red in Polystyrene; shows the absorption (excitation) and emission spectra of polystyrene polymer doped with 0.01, 0.02 and 0.05 wt% of Nile Red fluorescent dye. The dye absorbs the ambient light in the wavelength region from ~300 nm to ~570 nm and re-emits the light in the wavelength region from λ~570 nm to λ~670 nm. The maximum intensity of the fluorescent light occurs at λmax = 602 nm i.e. the polymer emits red light.

Figure 3: Absorption-Emission spectra of Coumarin 6 in Polystyrene; shows the absorption and emission spectra of polystyrene polymer doped with 0.07, 0.09 and 0.15 wt% of Coumarin fluorescent dye. The dye absorbs the ambient light in the wavelength region from λ ~ 250 nm to λ ~ 510 nm and re-emits the fluorescent light in the wavelength region from λ ~ 510nm to λ~ 560 nm. The maximum intensity for the fluorescent light occurs at λmax = 522 nm i.e. the polymer emits green light.

Figure 4: Absorption-Emission spectra of BisMSB in Polystyrene; shows the absorption and emission spectra of polystyrene polymer doped with 0.02 and 0.04 wt% of Bis MSB fluorescent dye. The dye absorbs the ambient light in the wavelength region from λ ~ 250 nm to λ ~ 410 nm and re-emits the fluorescent light in the wavelength region from λ ~ 410 nm to λ ~ 470 nm. The maximum intensity for the fluorescent light occurs at λmax = 430 nm i.e. the polymer emits blue light.

Figure 5: NR 0.04 wt% + C6 in Polystyrene vs. wavelength; shows the absorption and emission spectra of polystyrene polymer doped simultaneously with two fluorescent dye, Nile Red and Coumarin 6 respectively. Figure 5 is also an example of increasing the efficiency of red fluorescent light emission by using larger concentration of Coumarin 6 in the two component dye mixture. The relative efficiency for light generation increases by a factor of 2.4 when the Coumarine 6 dye concentration increases from 0.01 wt % to 0.04 wt % in the dye mixture. Figure 5 also shows that this increase in the efficiency is due to two factors; firstly due to increased absorption and secondly due to increased energy transfer of green light emission to red light emission.

Figure 6: Nile Red + Coumarine 6 in Polystyrene; summarises the relative efficiencies of ambient light absorption and fluorescent light emission as a function of the concentration of the dyes in the two component dye mixture in polystyrene host polymer. The largest efficiency for absorption and fluorescent light emission is obtained at 0.02 wt % of Coumarine 6 combined with 0.03 wt% Nile Red.

Figure 7: Absorption - Emission Area of Nile Red 0.04 % + Coumarine 6 + Bis MSB; describes the relative efficiencies for fluorescent light emission in a three component dye mixture in the polystyrene polymer host. The largest efficiency is obtained at the composition of 0.02 wt% Nile Red + 0.03 wt% Coumarin 6 + 0.01 wt % Bis MSB. Either increasing or decreasing the concentration of Bis MSB will result in a drop in efficiency for ligfht generation.

Figure 8: Quantum Yield of Coumarin 6 in polystyrene; describes the quantum Yield of coumarin 6 in polystyrene as a function of dye concentration. The optimum efficiency is obtained at 0.06 wt %.

Figure 9: Absorption - Emission Area of Coumarin 6 in Polystyrene; describes the relative magnitudes of absorption and fluorescent light emission as a function

of dye concentration. The comparison of Figure 8 and Figure 9 shows that the maximum efficiency for fluorescent light generation (at 0.06 wt%) is according to the maximum in the quantum yield (at 0.06wt%). Figure 9 also shows that the maximum in absorption is not necessarily according to the maximum in light emission.

Figure 10: Quantum Yield of Bis MSB in Polystyrene; describes the quantum yield of blue light generation as a function of dye concentration. The best efficiency is obtained at 0.035 wt %.

Figure 11. Arrangement for light scattering/Absorption measurements; this provides data for combined scattering and absorption profile within the fibre because the optical losses are due to two factors; a) absorption b) scattering.

Figure 12: Scattered light intensity from polycarbonate red and green fibers; describes the combined scattering / absorption data for fluorescent dye doped red and green polycarbonate (dye) optical fibres.

The ◆ * ▮ symbols refer to scattering / absorption data on polycarbonate fibres doped with increasing concentration of Coumarine 6 dye. These measurements are obtained by using an Ar ion laser (λ = 513 nm). The ▲ • ○ symbols refer to scattering/absorption data on polycarbonate fibres doped with increasing concentration of Nile Red dye. These measurements are obtained by using a He-Ne laser (λ = 632 nm).

All of the curves show the scattered light intensity as a function of the length l from the end of the fibre. The plots are linear in the semilogarithmic scale thus confirming the exponential nature of the light decay along the fibre. Generally the Red fibres (Nile Red NR doped polycarbonate) have more loss (measured at λ =632 nm) than the Green fibres (Coumarine 6, C6 doped polycarbonate), measured at λ = 513 nm. This is due to the dispersion of the refractive index (the refractive

index is smaller in the red spectral region than in the green spectral region). Figure 12 also shows the effect of the increase of the dye concentration on the scattering/absorption properties. As a particular dye concentration (Nile Red or Coumarine 6) increases, the scattering/absorption losses decrease (slope is becoming less) This is demonstrated by comparing the concentration of NR at 0.01 wt% and 0.03 wt %, and the comparison of C6 at at 0.01 wt% and 0.05 wt % respectively. The increased efficiency for fluorescent light collection therefore is due to the combined effect of increasing the dye concentration and the increase in the refractive index of the polymer (dye) guest host core.

Figure 13: Polycarbonate Fibres/ Polycarbonate with red/green laser; demonstrates the increase of the refractive index of the polycarbonate/C6 polymer/dye guest host system as a function of the C6 dye concentration. There is a linear dependence of the refractive index from n = 1.555 to n=1.585 on the dye concentration in the range between 0.035 wt% and 0.065 wt%.

Figure 14: Intensity of green/red fibre in sunlight while fibres are partially covered (normalised and an average of 7 measurements/ y-errors equal 2 sigma); demonstrates that the fluorescent light generation under sunlight excitation is saturated after ~ 60 cm length of the fibre. This is because the extra light generated in the middle of the fibre is scattered out or absorbed within the core. Comparison of Figure 14 with Figure 13, shows a good agreement, confirming the nature of light losses.

Figure 15: Structure of Light Emitting Polymer in combined reflective and transmissive mode; shows the structure of a polymer and the positioning of a dielectric stack relative to it.

Figure 16: Structure of Light Emitting Polymer in the Edge emitting Mode; shows the dielectric stack use in relation to an optical fibre polymer, where the dielectric stack mirror provides a band pass antireflection - reflection layer which

acts as an absorption free band pass filter for transmitting all of the spectral region of the ambient light for excitation of the fluorescent dye but reflects all of the emitted fluorescent light back to the sample.

Figure 17: GREEN Reflectance; demonstrates the Reflectance spectrum of the dielectric stack described in Table II.. The reflectance is nearly zero in the wavelength region from ~ 350 nm to 430 nm. This means that this spectral region of ambient light can be used for excitation of Coumarine 6. Comparison of Figure 17 with Figure 3. shows that the zero reflection region corresponds to the spectral region of absorption (excitation) region (~ 350 nm to 480 nm) for Coumarine 6). Alternatively, the reflectance is nearly 100 % for the spectral region from 450 nm to 550 nm. Comparison of Figure 14 with Figure 3 shows that the high reflectance region corresponds to the spectral region of green fluorescent light emitted by C6. This means that the emitted light is fully reflected back to the bulk of the flat panel.

Figure 18: GREEN1 Transmittance; demonstrates the Transmittance spectrum of the same dielectric stack as described in Table II. The Transmittance is ~ 80 % in the spectral region from ~ 350 nm to 430 nm. This allows the light to be transmitted for excitation. On the other hand, the transmittance is nearly zero in the spectral region from 450 nm to 550 nm. Comparison of Figure 18 with Figure 3 shows that the zero transmittance region corresponds to the spectral region of green fluorescent light emitted by C6. The panel looks deep blue in appearance as it transmits only blue light in the visible region, therefore, the contrast between the uncovered (bright green) and dielectric stack covered (dark blue) areas of the flat panel can be substantial, which is suited for display applications.

Figure 19: RED1 Reflectance; demonstrates the reflectance spectrum of a dielectric stack for a dielectric stack mirror designed with specification detailed in Table III. The reflectance has a nearly zero value in the spectral region from ~ 350 nm to ~ 500 nm. Comparison of Figure 19 with Figure 2 shows that the zero

reflectance region corresponds to the absorption region of the Nile Red dye in Polystyrene. Alternatively, nearly 100 % reflectance region (~ 530 nm to 650 nm) corresponds to the light emission spectral region of the Nile Red in Polystyrene.

Figure 20: RED1 Transmittance; demonstrates the transmittance spectrum of the same dielectric stack as described in Table III. Comparison of Figure 20 with Figure 2. confirms that the high transmittance region corresponds to the spectral region of Nile Red absorption in Polystyrene.

Figures 21, 22 and 23 show a constant contrast of fluorescent polymer based display; where Figure 21 shows the display in full sunlight conditions, Figure 22 shows the display in cloudy conditions and Figure 23 shows the display in late evening condition (two hours after sunset). The photographs shown in figures 20, 21 and 22 demonstrate the concept of "constant contrast" between the light emitted from the end of the fibres and the intensity of the ambient light.

It is already stated earlier that the contrast between the light power flux emitted from the end of the fibre and the ambient light power flux is constant because this property does not depend on the ambient light intensity. The photos clearly show that the contrast between the "NAPIER" sign, the blue line above the Napier sign and the ambient light intensity remains fairly constant down to very low level of illumination (2 hours after sunset).

Additionally, any transparent polymer can be used as core and/or cladding material. In practice the choice is limited by the compatibility of the polymer core with the fluorescent dye and the requirement for employing high refractive index material for the polymer core and low refractive index material for the polymer cladding. Polymers are favoured over glasses for several reasons such as low temperature processing capability (for fibres and polymer mouldings), compatibility with organic fluorescent dyes and good mechanical properties (strength and flexibility).

In principle, any fluorescent dye compatible with any transparent polymer can be used for this purpose. In practice the choice is limited by the compatibility of the fluorescent dye with the polymer core, the required colour, and the stability and lifetime. The contrast between the light power density emitted from the polymer and the light power density of the ambient light remains constant because this parameter is not effected by ambient light conditions as long as they are above a critical level and instead relies on the material parameters.

Typical examples for the core are; polymethylmethacrylate (PMMA), polystyrene, polycarbonate, cyclic olefin copolymers, or any similar transparent polymer, commercially available as either monomers of polymers from Aldrich, BASF, Bayer, GE Plastics, Ticona or other suppliers.

Typical examples for the fluorescent dye are; Coumarin 6 (green fluorescent dye) , Coumarin 7 (green fluorescent dye), Coumarine 314 (green fluorescent dye) 1,8-Diphenyl-1,3,5,7, - octatetrene (yellow fluorescent dye) Nile Red (red fluorescent dye), Bis-MSB (blue fluorescent dye), Cresyl Violet Perchlorate (red fluorescent dye), Sulforhodamine 101(red fluorescent dye) , Sulforhodamine 640 (red fluorescent dye), commercially available from Aldrich or Exciton, or other suppliers.

The fluorescent dyes can be incorporated into the core polymers by any suitable method, including:

1. Dissolving the dyes in the monomer and then carrying out bulk polymerisation to produce a cast sheet or rod preform (for fibre drawing).
2. Melt compounding of dyes into polymer using either a batch internal mixer, or continuous compounding equipment (such a single screw extruder or a twin screw extruder).

Typical initiators such as AIBN and Benzoyl Peroxide are also available commercially from Aldrich or other suppliers.

Method of polymerisation:

Polymerisation is carried out directly from the monomer (with dye dissolved in it) or more often from a monomer-polymer syrup approximately 20-40 weight percent of polymer. Prior to polymerisation, the fluorescent dye is dissolved in the monomer. This is a preferred method for dissolution because of the simplicity of the process and because there is no need to apply an extra solvent which would decrease the efficiency of the dye in the host matrix.

The fluorescent dye concentration in the monomer is in the range of 0.005 weight % to 0.2 weight %. The polymerisation is carried out in the temperature range from 20°C to 50°C in steps over 5 hours and keeping the material for 12 hours at 50°C. The slow process helps control the exotherm effect during polymerisation. If the material is overheated during the polymerisation, volatile monomer can produce bubbles inside the material resulting in defects and optical non-uniformities within the final polymer product. Therefore it is important to control the polymerisation temperature range. Alternatively other polymerisation techniques may be used, for example using ultra-violet light. By such a method rods can be cast in glass tubes to produce polymer (dye) rods approximately 25 mm in diameter and 1 metre in length suitable for drawing into optical fibres.

Optical fibre drawing of the rods can be based on the rod in tube method using a process similar to that used for glass optical fibre (though at a very much lower temperature). In the preferred embodiment a polystyrene (Coumarin 6) rod is placed inside a PMMA tube. The rod in tube structure is surrounded by an oven which has a temperature around 265°C. The oven heats up the rod in tube structure and consequently the viscosity of both the rod and the tube decreases to a value close to that of the liquid phase. Simultaneously, with the heating, a tension is applied via a wheel and belt system to the rod in tube structure. The combined effect of temperature and tension results in fibres drawn from the rod in tube. The

internal core is drawn from the rod and the outer cladding is drawn from the tube. Polystyrene has a higher refractive index so it is used as the core material and polymethylmethactrylate has a lower refractive index so it is used as the cladding material.

Other techniques can also be used to produce the polymer (dye) -polymer, core-clad fibre, such as continuous extrusion. The core is extruded and the cladding applied by: coextrusion at the die-head; downline by crosshead die extrusion (similar to that used for wire covering); or solution coating.
A typical example of co-extruded fibre is polycarbonate core with fluoropolymer cladding, but the same method can be used for polystyrene fibres clad with polymethylmethacrylate.

In general a polycarbonate (dye) core with a suitable low refractive index fluoropolymer such as FEP or amorphous Teflon, (both produced by DuPont) for cladding can be used to make fluorescent optical fibres.

Table I illustrates several examples giving values of light power flux from optical fibres at an ambient sunlight power flux of Ps = 0.05 W/m^2.

Examples:

As a first example of the invention Figure 1 describes the structure of the light emitting polymer in reflective mode. The transparent polymer is chemically doped or blended with a fluorescent dye. The fluorescent dye should have a high quantum efficiency for converting natural light or indoor light into some visible colour. The bottom surface and edges of the polymer are covered with a highly reflective additional layer which acts as a mirror and ensures that all light entering through the top surface is fully reflected back into the polymer.

The top surface of the polymer is covered with a dielectric stack mirror which

comprises two dielectric films with alternating high and low refractive indices. This dielectric stack serves as an interference filter allowing 100% transmission of light from the air to the polymer for the wavelengths used for excitation of the fluorescent dyes doped within the polymer. The dielectric stack however has a near 100% reflection for light wavelengths emitted from the fluorescent dyes doped within the polymer. The dielectric layers can be vacuum evaporated, spin coated or sputtered onto the surface of the polymer.

Alternatively, thin films of two different polymers with two different refractive indices can also be applied to the polymer surface sequentially vacuum pressed and/or thermally treated for each layer. This method allows larger areas to be covered by the dielectric stack mirror. Alternatively, cladding can also be applied for the same purpose although the efficiency is not as good as with dielectric stack mirror.

This arrangement, coupled with the fact that the polymer layer itself acts as a guide for light generated inside the polymer (polymer refractive index about 1.5, air refractive index about 1), ensures that the polymer layer acts as a "light-trap" for wavelengths used for excitation and light emission from the fluorescent dye embedded in the polymer matrix.

On the other hand the fluorescent light emitted from the dye can be coupled out from the polymer at the top surface by emitting or removing the dielectric stack mirror at a given surface area and by making an uneven or grated surface at the polymer/air interface. The grating structure should be maximised for maximum diffraction for the emitted fluorescent light wavelength.

The intensity of the fluorescent light I1 ($mW/cm^2/nm$) emitted from the dye doped polymer (at a given dye concentration) at the grated surface is linearly proportional to the R1 at a given dye concentration;

$I1 \sim R1$ = total light collecting surface area (cm^2) / total grated area (cm^2)

This means that the larger ratio (R1) produces more fluorescent light. On the other hand, the contrast of the display defined as the intensity of the fluorescent light from the grated surface divided by the intensity of the ambient light is constant because this ratio is only dependent on the geometry of the display device (at a given dye concentration). This feature is particularly useful under variable ambient light conditions.

The device described above can be used to display letters, characters, symbols etc by using natural or artificial light from the environment and converting this light into a characteristic colour of fluorescent light and directing it (by total internal reflection or by interference) into the display area. By selecting the appropriate dye-polymer combination and by maximising the ratio of light collecting area divided by light emitting display area of a contrast of 10:1 or larger can be achieved for display purposes. This contrast is independent from the ambient lighting conditions. It is emphasised again that this device does not consume any electrical power. However, the device will not provide enough light for the display purposes when the ambient light intensity decreases below a critical level. In this case a conventional light source can be switched on to provide light for excitation and consequently displaying information. This electrical source does not illuminate the display directly and works in an indirect fashion.

An alternative example of the invention is shown in Figure 15. By replacement of the bottom mirror layer with a dielectric stack mirror, identical to the one applied to the top surface, a combined reflective and transmissive mode of light collection and display operation is also possible. The principle of operation is shown in Figure 15. A combined reflective and transmissive mode of operation is particularly useful for displays fixed on the inside of shop windows. Again as in the reflective mode of operation, the contrast for displaying information is independent of ambient lighting conditions.

A third mode of operation is shown in Figure 15. A dielectric stack mirror is applied on both sides of the transparent polymer-dye matrix but no side mirrors are applied. Consequently the fluorescent light generated inside the polymer will be waveguided towards the edges. The value of fluorescent light intensity 12 ($mW/cm^2/nm$) at the edges is directly proportional to the R2;

I2 ~ R2 = total light collecting surface area (cm^2) / edge area (cm^2) at a given concentration of fluorescent dye.

In summary the devices described above can be used to display letters, characters, symbols etc by using natural or artificial light from the environment and converting this light into a characteristic colour of fluorescent light and directing it by total internal reflection or by interference into the display area. Through selection of the appropriate dye polymer combination and by maximising the ratio of light collecting area dividing by light emitting display a contrast of 10:1 or larger can be achieved for display purposes. This contrast being independent from ambient lighting conditions.

The key elements of the invention are;

A method in which fluorescent dye doped polymer based optical wave-guide structures such as optical fibres, arrays of fibres, woven arrays of fibres, rods, sheets, folded sheets and moulded shapes of arbitrary geometry can be used to fabricate display and/or illumination elements for a range of applications such as road signs, traffic signs, safety signs, fixed advertisements, animation, dynamic display elements, toys, games lamps etc., without the usage of external electrical power thus saving energy.

A method in which display elements fabricated from fluorescent dye doped polymer wave-guide structures can provide a constant contrast between the light

power flux emitted from the wave-guide structure and the light power flux of the ambient light. This is a unique feature as compared to conventional electrically powered display elements.

A method in which a dielectric stack mirror layer fabricated on the surface of flat panels, sheets, and/or moulded surfaces and any other optical elements described above can be used to improve the efficiency and the contrast of those optical elements.

A method in which the efficiency of the fluorescent dye doped polymer based optical wave-guide structures can be improved by optimising the refractive index of the cladding layer.

A method in which fluorescent dye doped polymer based optical wave-guide structures can provide optical amplification of the emitted fluorescent light by optimising the wave-guide geometry, the composition of the dye (or dye mixtures) the dye concentrations, and the polymer host.

A method in which fluorescent dye doped polymer based optical wave-guide structures can provide a range of colours in the visible spectrum (from red to blue) by absorbing the ambient light (artificial and/or sunlight) and converting them into the required colour specification depending on the specific choice of the dye and the polymer.

Methods for a range of specific applications using fluorescent dye doped optical wave-guide structures which are detailed in the application section

Methods for a range of applications in which a range of specific applications using fluorescent dye doped optical wave-guide structures can be combined with established generic technologies.

Applications:

'24 hour' road signs.

An array of light-emitting rods, each one having a shuttering mechanism at its end, is housed in an enclosure, along with a solar panel and battery which is used to power a light during the hours of darkness. This light is activated by a light sensor and provides an appropriate spectrum for energy conversion by the rods. The solar panel charges the battery during the daylight hours, when the light source is not required. An example of such a device and the principles involved, is shown in Figure 23.

24 hour' traffic lights.

Using the fibres' qualities of producing red, green and amber fluorescent colours, a system can be designed to simulate traffic lights, with the sequence control circuitry, light sensor and night light powered using the solar panel / battery combination (as detailed in ''24 hour' road signs' application). An example of such a device and the principles involved, is shown in Figure 24.

Fixed advertisements:

These can take one of several primary forms, or combinations of these forms. The first form is that of fibres / rods, as used in the '24 hour road signs, but without using any shuttering process. i.e. they continuously display an unchanging image, whether that image is in the form of characters, symbols, logos, or in the style of a picture, or in some combination of these.
The lengths of fibres / rods would not be shown, only the artwork as would be seen from the front is displayed.

The second form is that of a contoured sheet format, where the edges of the sheet emit light and form the display; this can take the form of characters, shapes, logos.

The third format is that of a sheet which has a dielectric stack mirror coated onto the surface. An example of such a device and the principles involved, is shown in Figure 25. The purpose of the coating is to allow sunlight to penetrate into the sheet material, and to energise the incorporated dye, but then to trap the fluorescent light produced within the sheet, by reflecting these fluorescent wavelengths back from the surface coating. By selectively removing parts of the coating, light is permitted to escape from the sheet, and this forms the basis of a display. In this way, characters, symbols, logos, diagrams etc. can be produced.

Operation of doped material during the hours of darkness can also be achieved using material which can absorb light from street lights (from the sodium D lines 589.0 and 589.6 nm) and convert it to red fluorescent light. Typical materials, along with their maximum excitation wavelength ($\lambda_{exc.max}$) and their maximum emission wavelength ($\lambda_{em.max.}$) are :

Material	$\lambda_{exc.max}$	$\lambda_{em.max.}$
cresyl violate perchlorate	593	615
oxazine 4 perchlorate	610	625
sulforhodamine 101	578	605
LD 690 perchlorate	616	625

Toys.

The integration of this technology into toys can take on several forms. Fibres can be transformed into flowers, where the long stem gathers the sunlight and the head / petals etc. emit the fluorescent light. Doll's hair and cat's whiskers can also use this approach.

Sheet format can be used to produce structures which are colourful and strong, yet virtually transparent, where its edges emit fluorescent light e.g. a doll's house, where the interior decoration / furniture can be viewed through the exterior walls, and the light is emitted from around the windows / door / roof edges etc. to give the impression of a 'magic' house.

Moulding of the material into different shapes can be done. These shapes may either be hollow or solid, and could produce a range of toys which are tough and durable, yet can incorporate special features, such as 'shining' eyes, ears, a laser gun which emits 'laser' light, or a number of other accessories for toys / movie theme characters.

Use can be made of the dielectric stack mirror onto these materials to produce numerous effects. e.g. a car track can be designed to reveal an effect similar to 'shining' cat's eyes; a toy garage can have its sign illuminated; lights illuminating the floor of a small swimming pool; windows which appear to have a light switched on inside the room of a toy house etc.

Games which utilise the capture of sunlight, with the subsequent emission of a range of visible colours can be designed.

As the peg is pushed through the sheet of light absorbing material, it comes into contact with the sheet of light-emitting material, and this allows the light to pass into the peg, which then becomes illuminated.

Safety.

Fibres have a certain amount of light 'leaking' out along its length. This is dependant upon the refractive indices of both the doped material and the substance in contact with this material, and also on the amount the material is bent. From these facts, there are three techniques which can be applied to improve peoples'

safety in dark conditions or when poor visibility exists.

By capturing sufficient sunlight into a section of the fibre which is exposed to the sun, then light will leak out gradually along that part of its length which is placed within the darkened conditions. In this way, anyone can follow the illuminated fibre out of the darkened room to safety. An example of such a device and the principles involved, is shown in Figure 27.

The second and third techniques involve the same principles of injecting light into the fibre as the one just described. However, the second technique makes use of the fact that a bend in the fibre will cause an increased amount of light to leak out. This may be useful where an increased amount of light is necessary in order to be seen (e.g. in smoke-filled rooms). Also, the spacings between the bends can be utilised to inform the people which is the quickest way out of the room (e.g. decreasing spaces indicates the way out).

The third technique makes use of the substance in contact with the doped material. If a substance which has a refractive index similar to the doped material is placed in contact with it, then an increased quantity of light will leak out. This can both be used to make that area more easily visible and also to provide information. (e.g. the geometrical shape of the substance (e.g. →) can be selected to guide the person from the room in the easiest manner.)

Two other methods of capturing light from outside a building and introducing it into the inside are by using a sheet on the outside to collect the light and by attaching fibres to the edges of the sheet, the light is coupled to the fibres, which can then be fed into the inside of the building. The other method of transferring light to the inside of a building is by using a longer length(s) of fibre / rod on the outside and passing the fibre into the interior.

Another safety application could be as sails , or sail coating, so that the edge of the

sail becomes more easily visible in misty, foggy conditions, or when the light level is poor.

People who go out jogging in poor conditions could also benefit from wearing an outer garment which is made from, or has patches of, this material. Jogging shoes could also benefit in a similar way. They would be more easily seen by motorists, and so help to avoid accidents.

Cars, motorcycles and cyclists can also benefit from fitting sections of this fluorescent material onto their external surfaces, so that other motorists / pedestrians can see them more easily. This can take the form of a warning strip which can be seen on e.g. all four sides of a car.

Airport runway illumination.

An application of light-emitting fibres / rods is that of airport runway lights, where a series of these rods are placed on either side of the runway, and each rod is suitably angled towards the incoming aircraft. An example of such a device and the principles involved, is shown in Figure 28.

This application would be for daytime use, and the existing system of runway lighting would be used during the hours of darkness.

Fashion accessories.

A range of accessories can be designed to take advantages of the materials' light-emitting qualities. These include raincoats with edges that shine, clothes or cloth, patches, broches, rings, jewellery, necklaces, bangles etc.

Other types of concepts include candles with a light-emitting 'flame' and Christmas tree lights.

24 hour bus arrival scheduler.

This is a communication device, mounted at a bus stop, which informs potential passengers when the arrival of the next bus(es) is due. It takes the form of a satellite communications receiver / decoder, linked up to a display which consists of a doped material which can operate even during the hours of darkness. This can be achieved using material which can absorb light from street lights (from the sodium D lines 589.0 and 589.6 nm) and convert it to red fluorescent light. A solar panel can be used to charge a battery which provides power for the communications receiver and the electronically-controlled shuttering for the display. A back-up night light can be provided to enhance the visibility of the display in conditions where the street lights are poor. This would also be powered by the battery.

Claims

1. A fluorescent dye doped polymer for use as an optical fibre, a film or sheet wherein an optically transparent polymer is doped or blended with organic fluorescent dye molecules for use in visual display wherein fluorescent light is generated when artificial ambient light, daylight or sunlight enters the doped polymer or optical fibres.

2. A fluorescent dye doped polymer, as claimed in Claim 1, wherein the transparent polymer is chosen from the group comprising PMMA, polycarbonate and polystyrene.

3. A fluorescent dye doped polymer, as claimed in Claim 1, wherein any organic fluorescent dye is used.

4. A fluorescent dye doped polymer, as claimed in Claim 1, wherein the fluorescent dye molecules are chosen from a group comprising: PBD, Bis-MSB, 3-3'-diethyloxycarbocyanine-iodide and cresyl violet 670 perchlorate.

5. A fluorescent dye doped polymer, as claimed in Claim 1, where the polymer forms an optical fibre, the radius of such a fibre is between 0.25 and 0.70 x 10^{-2} meters and the length of the fibre is between 0.2 and 1.6 meters.

6. An fluorescent dye doped polymer claimed in Claim 5 wherein the magnitude of the fluorescent light emitted from such a fibre is given by the equation $Aa/Ae = 2L/r$ wherein Aa is the surface area of the fibre and Ae is the area at which the fluorescent light is emitted.

7. A fluorescent dye doped polymer, as claimed any of Claims 1 to 6, for use as a display pixel, where artificial ambient light or sunlight provides excitation sources.

8. A display comprising a fluorescent dye doped polymer, as claimed in any of the preceding claims, consisting of a plurality of fibres, which may include individual fibres which emit an alternative, predetermined colour of light, whereby the light is defined by the fluorescent dye which is doped within the polymer.

9. A display as claimed in Claim 8, in a flat panel conformation wherein the bottom surfaces and edges of the polymer film are covered with a highly reflective additional layer which acts as a mirror performing the role of total internal reflection of all light entering into the polymer.

10. A flat panel display as claimed in Claim 9, whereby the top surface of the polymer is covered with a dielectric stack mirror.

11. A flat panel display as claimed in Claim 9 or 10, wherein the stack is constituted of an alternating sequence of two dielectric films with alternately high and low refractive indices.

12. A flat panel display as claimed in Claim 10, comprising a dielectric stack whereby the composition of this dielectric stack acts as an interference filter to allow substantially 100% transmission of light from air into the polymer for wavelengths used for excitation of the dye.

13. A flat panel display as claimed in any of Claims 9 to 11, where the stack has substantially 100% reflection for light wavelengths emitted from the fluorescent dyes, the dielectric layers have been vacuum evaporated, spin coated or sputtered onto the surface of the polymer.

14. A display as claimed in Claim 12 , whereby thin films of two different polymers, with the two different refractive indices, can be applied to the

polymer surface sequentially and vacuum pressed and/or thermally treated for each layer.

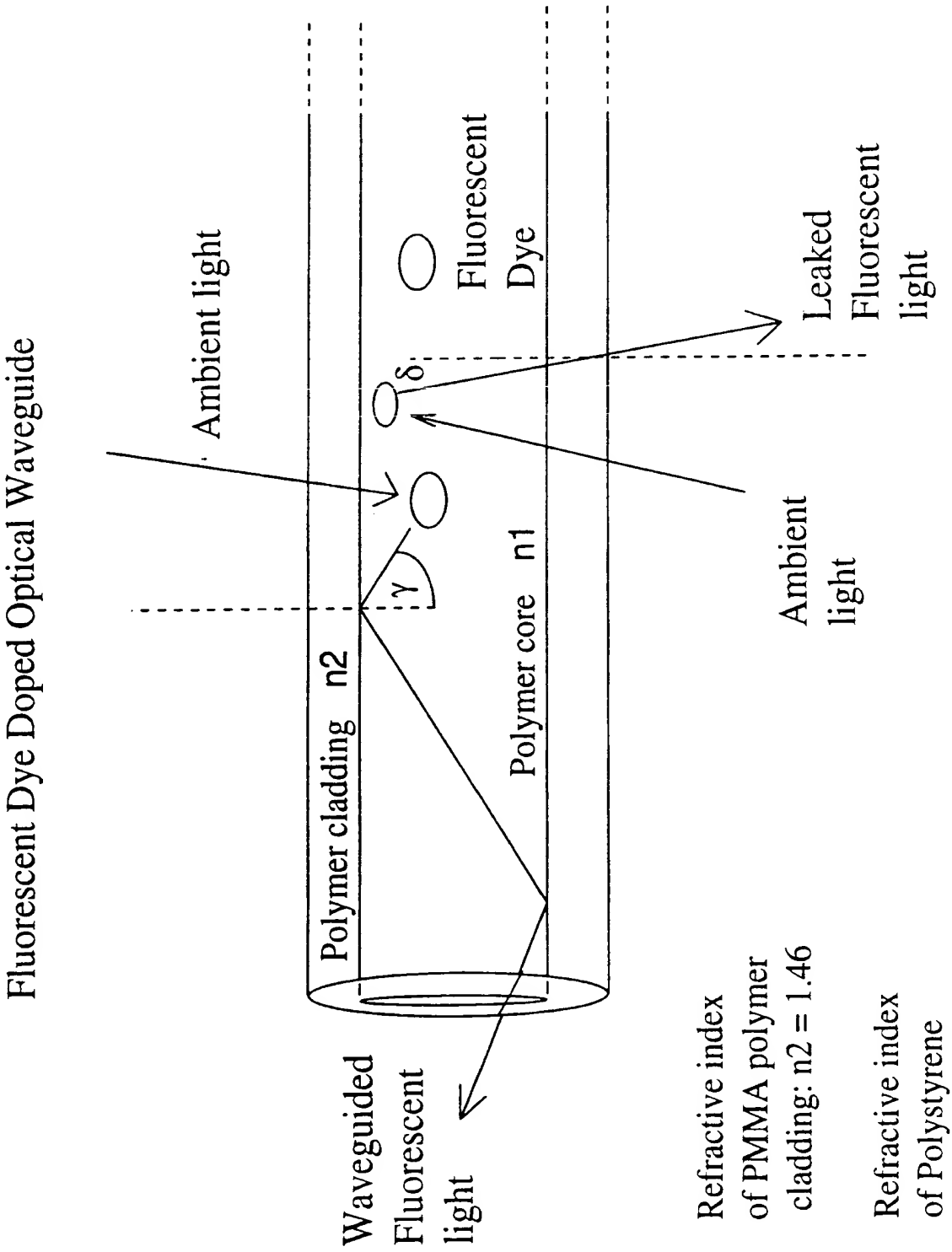

Fluorescent Dye Doped Optical Waveguide
Ambient light
Fluorescent Dye
Leaked Fluorescent light
δ
γ
Ambient light
Polymer cladding n2
Polymer core n1
Waveguided Fluorescent light
Refractive index of PMMA polymer cladding: n2 = 1.46
Refractive index of Polystyrene core: n1 = 1.6

Fig 1

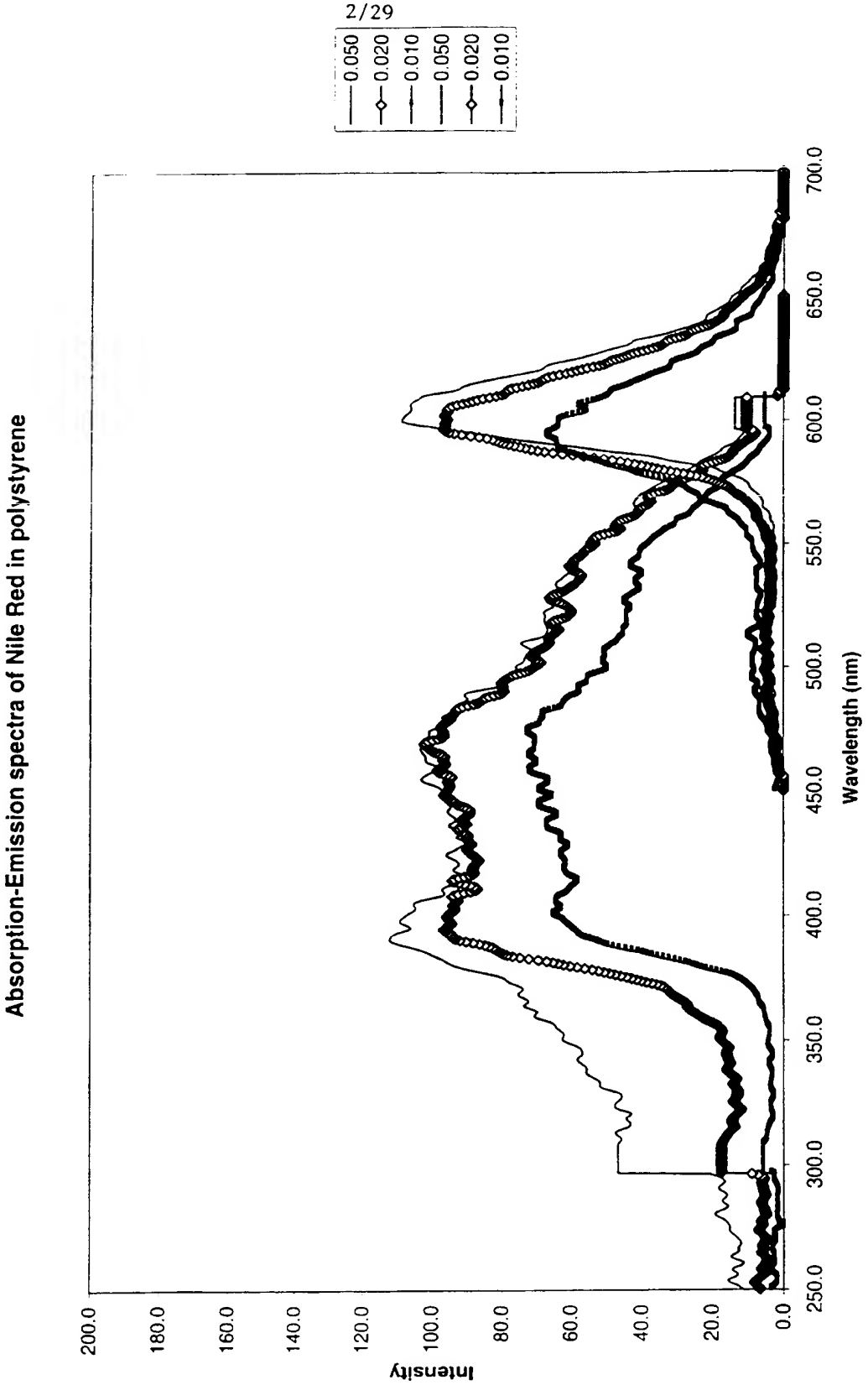

Absorption-Emission spectra of Nile Red in polystyrene
0.050
0.020
0.010
0.050
0.020
0.010
Intensity
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
250.0
300.0
350.0
400.0
450.0
500.0
550.0
600.0
650.0
700.0
Wavelength (nm)

Fig 2

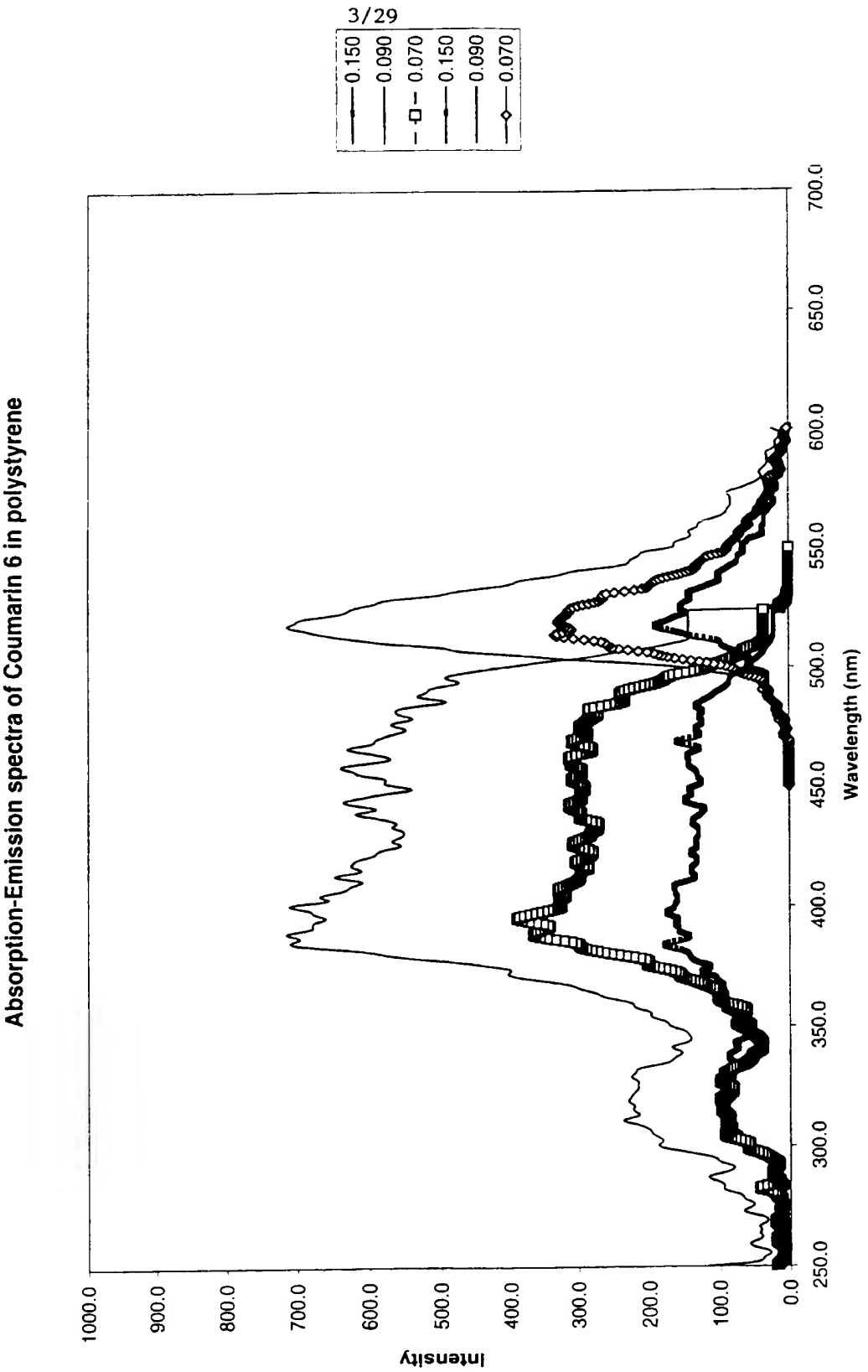

Absorption-Emission spectra of Coumarin 6 in polystyrene
0.150
0.090
0.070
0.150
0.090
0.070
Intensity
1000.0
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
250.0
300.0
350.0
400.0
450.0
500.0
550.0
600.0
650.0
700.0
Wavelength (nm)

Fig 3

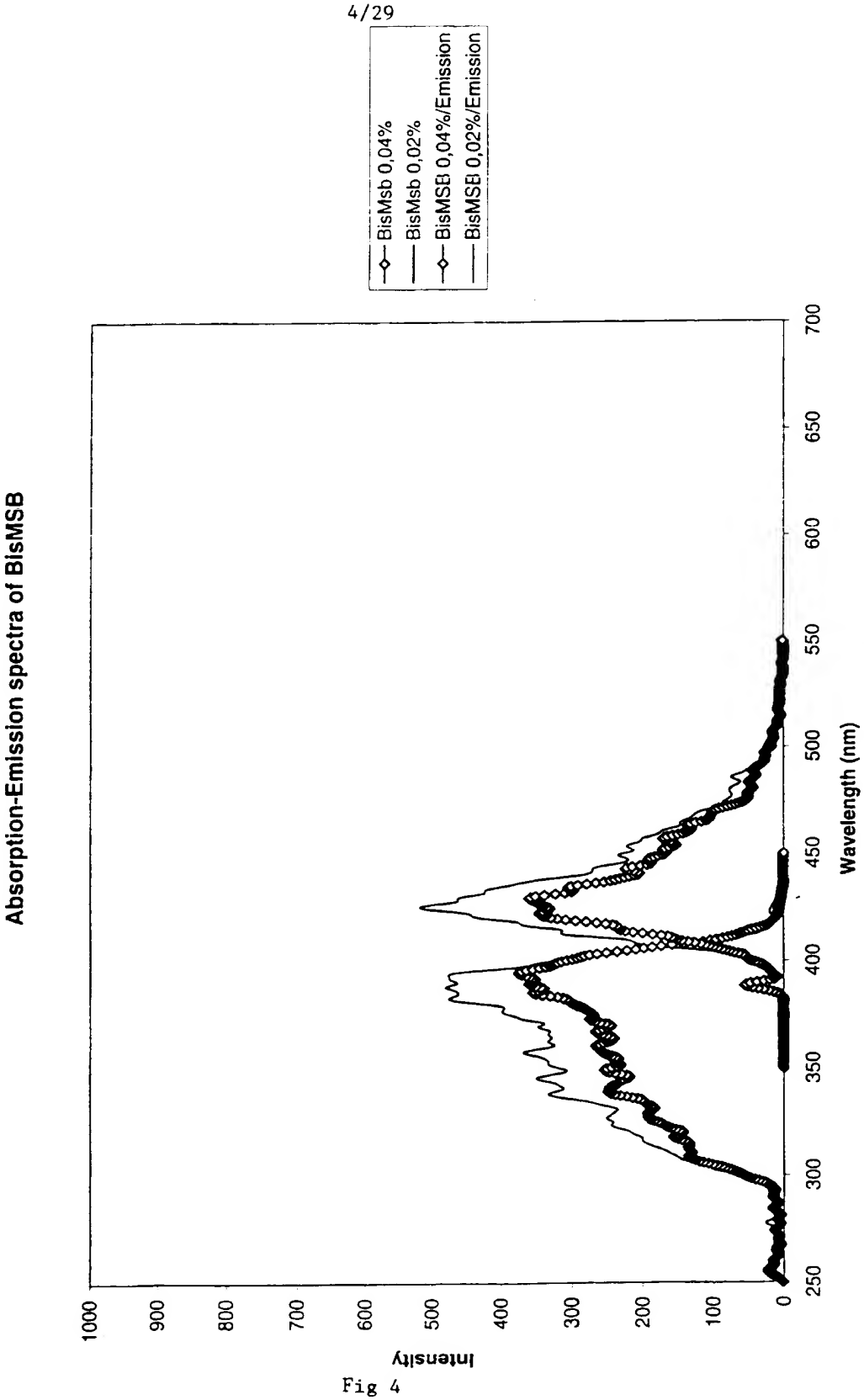

Absorption-Emission spectra of BisMSB
BisMsb 0,04%
BisMsb 0,02%
BisMSB 0,04%/Emission
BisMSB 0,02%/Emission
Intensity
1000
900
800
700
600
500
400
300
200
100
0
250
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Fig 4

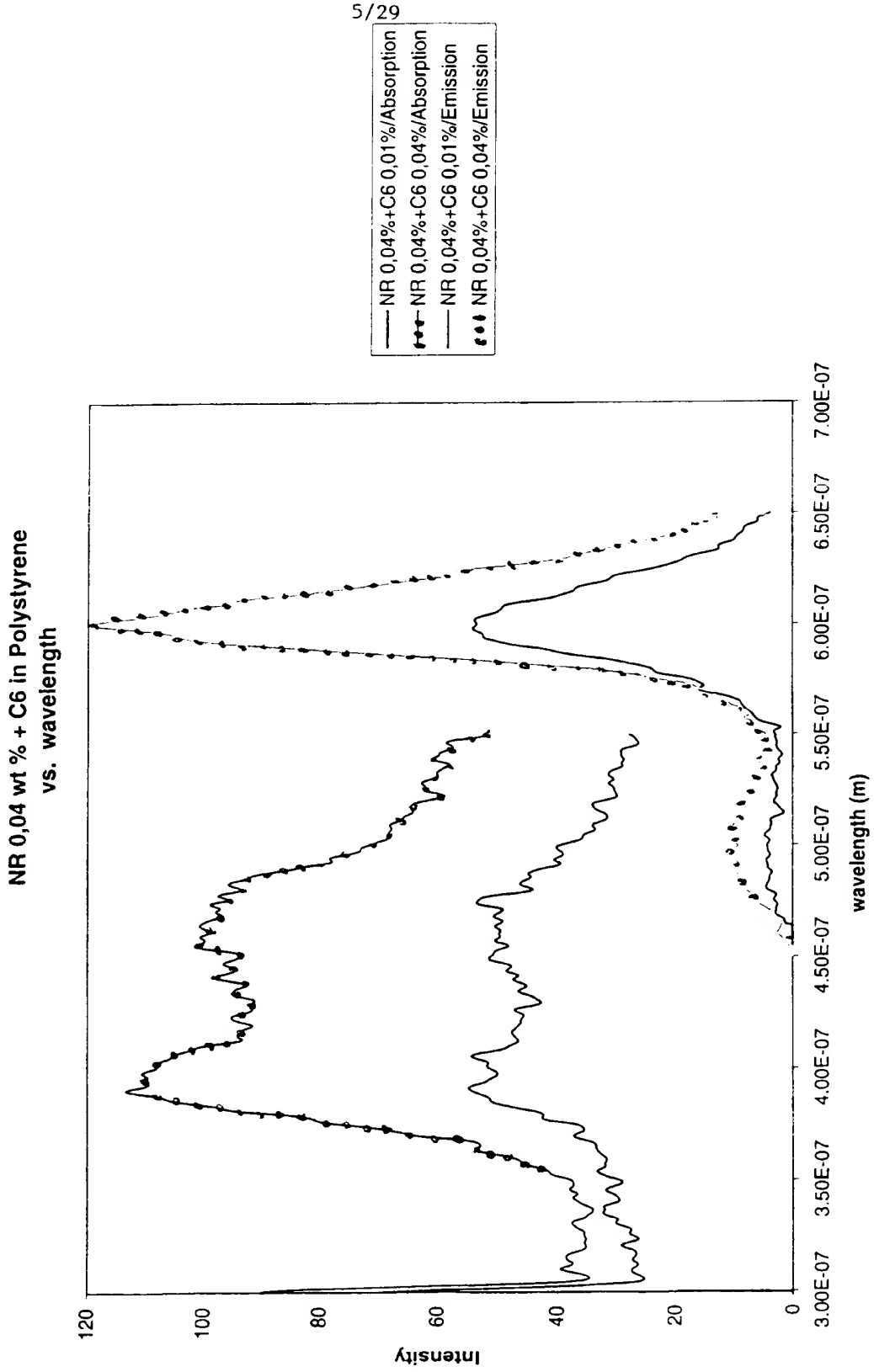

NR 0,04%+C6 0,01%/Absorption
NR 0,04%+C6 0,04%/Absorption
NR 0,04%+C6 0,01%/Emission
NR 0,04%+C6 0,04%/Emission
NR 0,04 wt % + C6 in Polystyrene
vs. wavelength
Intensity
wavelength (m)
120
100
80
60
40
20
0
3.00E-07
3.50E-07
4.00E-07
4.50E-07
5.00E-07
5.50E-07
6.00E-07
6.50E-07
7.00E-07

Fig 5

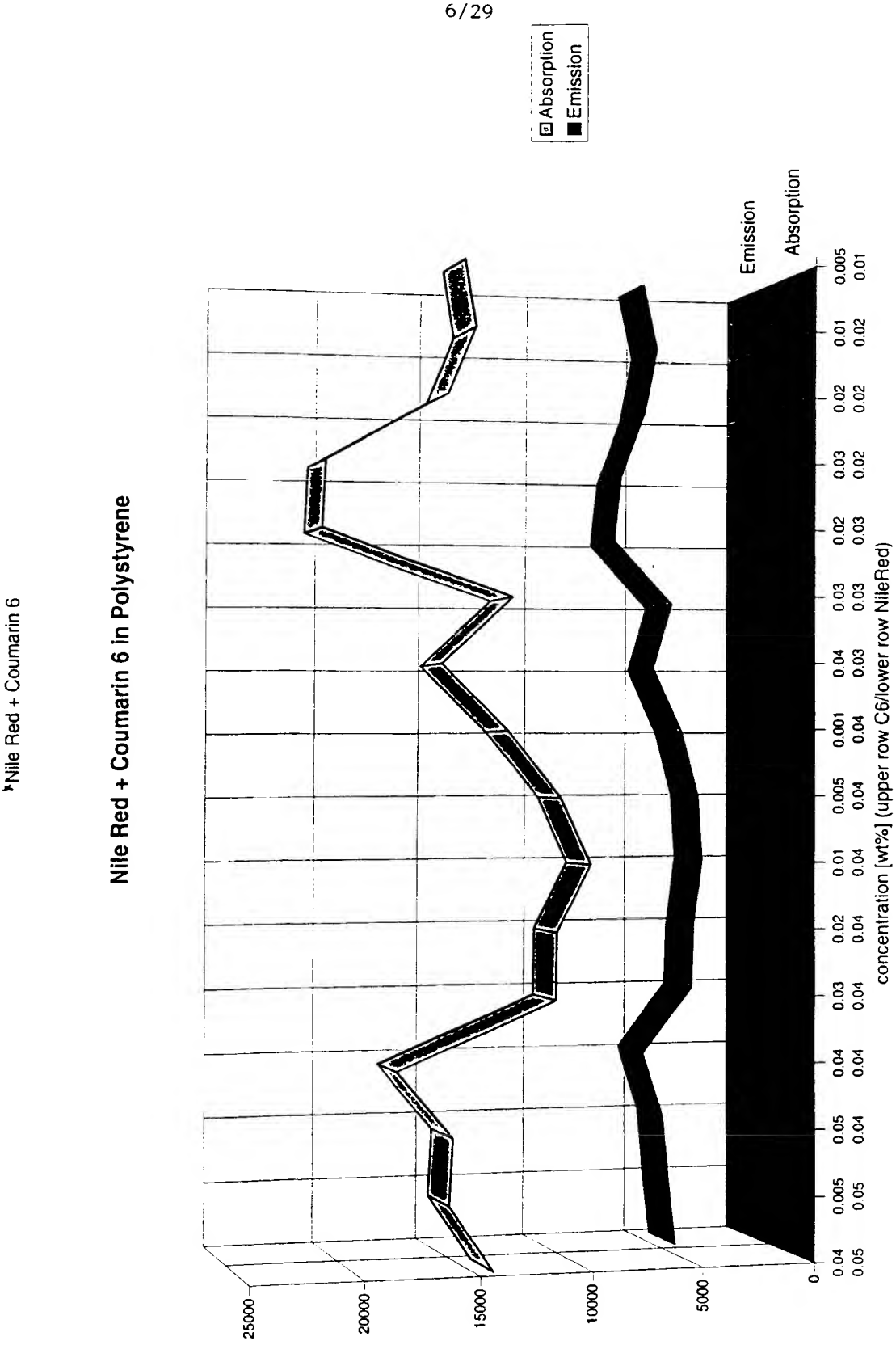

Nile Red + Coumarin 6
Nile Red + Coumarin 6 in Polystyrene
Absorption
Emission
Emission
Absorption
25000
20000
15000
10000
5000
0
0.04 0.005 0.05 0.04 0.04 0.03 0.04 0.02 0.04 0.01 0.04 0.005 0.04 0.001 0.04 0.03 0.03 0.02 0.03 0.02 0.02 0.01 0.02 0.005 0.01
0.05 0.05 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.04 0.03 0.03 0.03 0.03 0.02 0.02 0.02 0.02 0.01
concentration [wt%] (upper row C6/lower row NileRed)

Fig 6

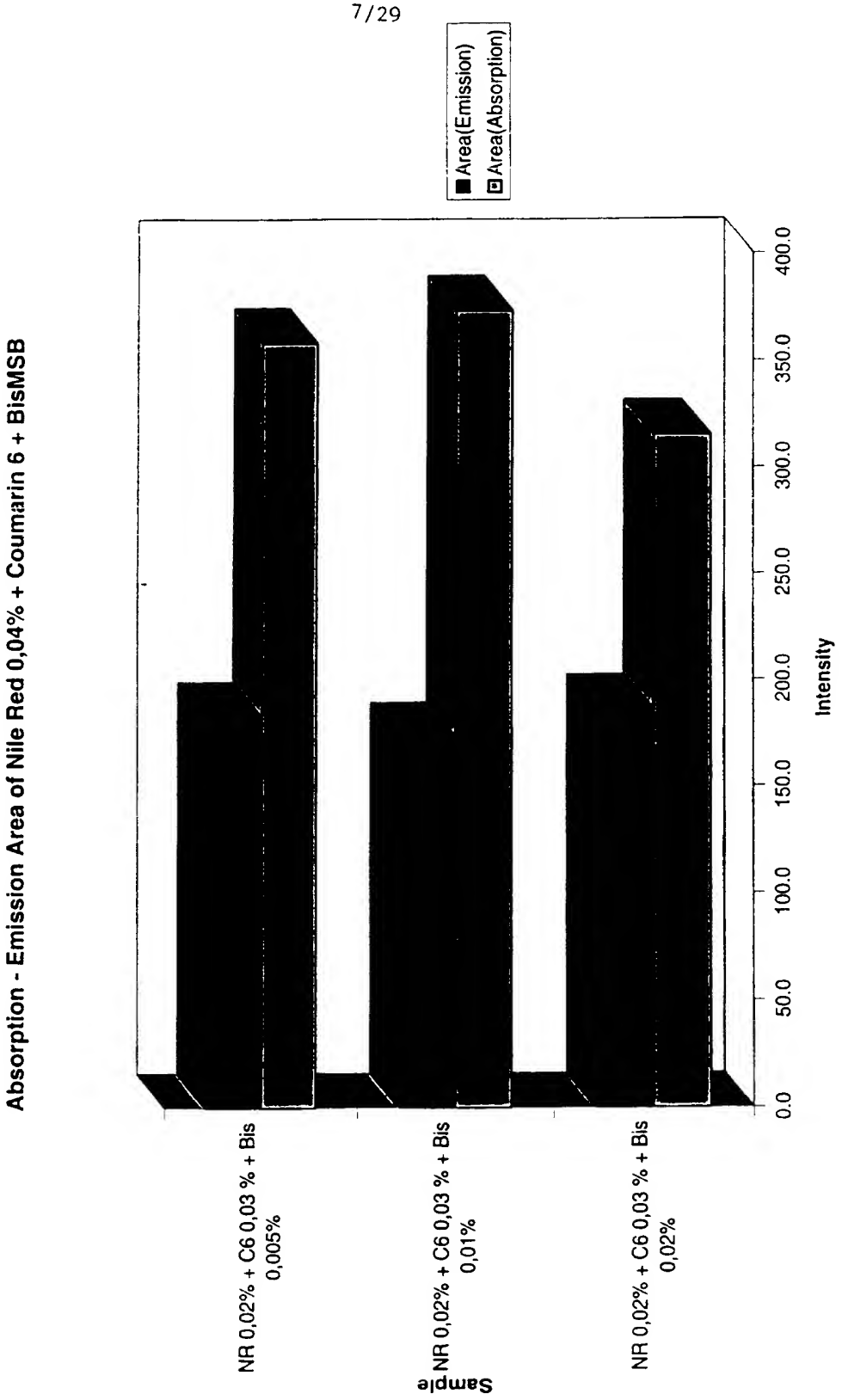

Absorption - Emission Area of Nile Red 0,04% + Coumarin 6 + BisMSB
Area(Emission)
Area(Absorption)
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
Intensity
NR 0,02% + C6 0,03 % + Bis 0,005%
NR 0,02% + C6 0,03 % + Bis 0,01%
NR 0,02% + C6 0,03 % + Bis 0,02%
Sample

Fig 7

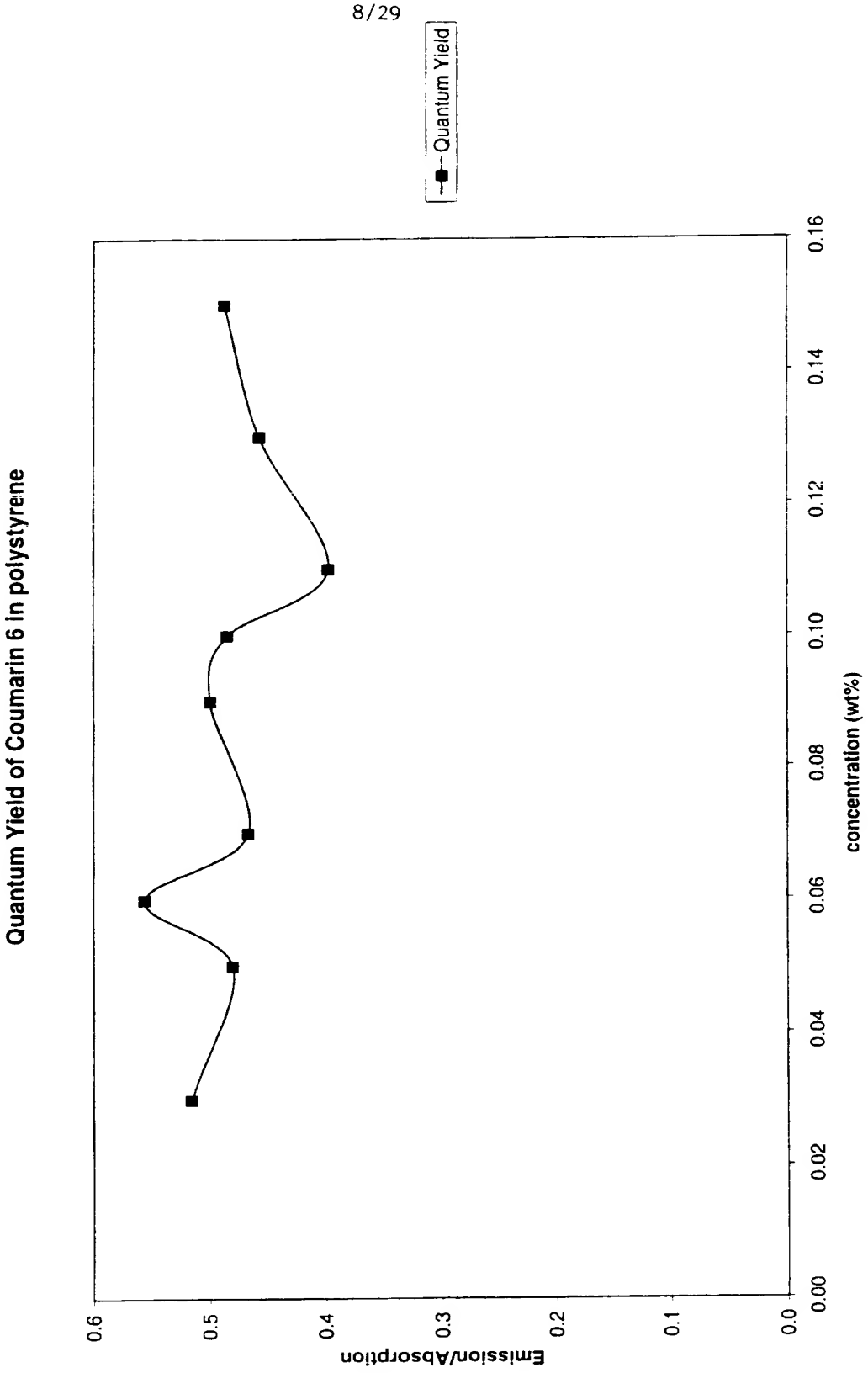

Quantum Yield of Coumarin 6 in polystyrene
Quantum Yield
Emission/Absorption
0.0
0.1
0.2
0.3
0.4
0.5
0.6
concentration (wt%)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16

Fig 8

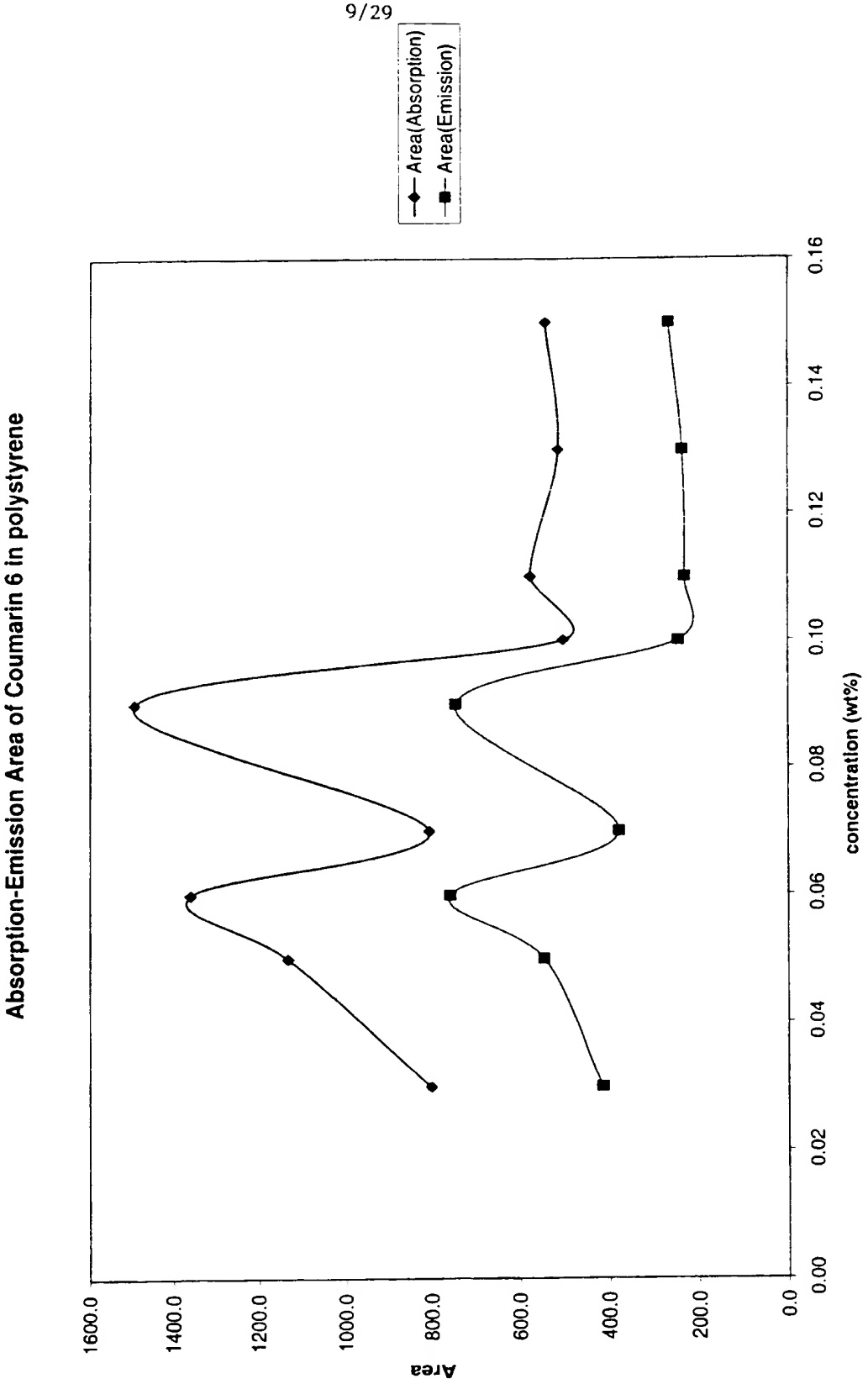

Absorption-Emission Area of Coumarin 6 in polystyrene
Area(Absorption)
Area(Emission)
Area
concentration (wt%)
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
1400.0
1600.0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16

Fig 9

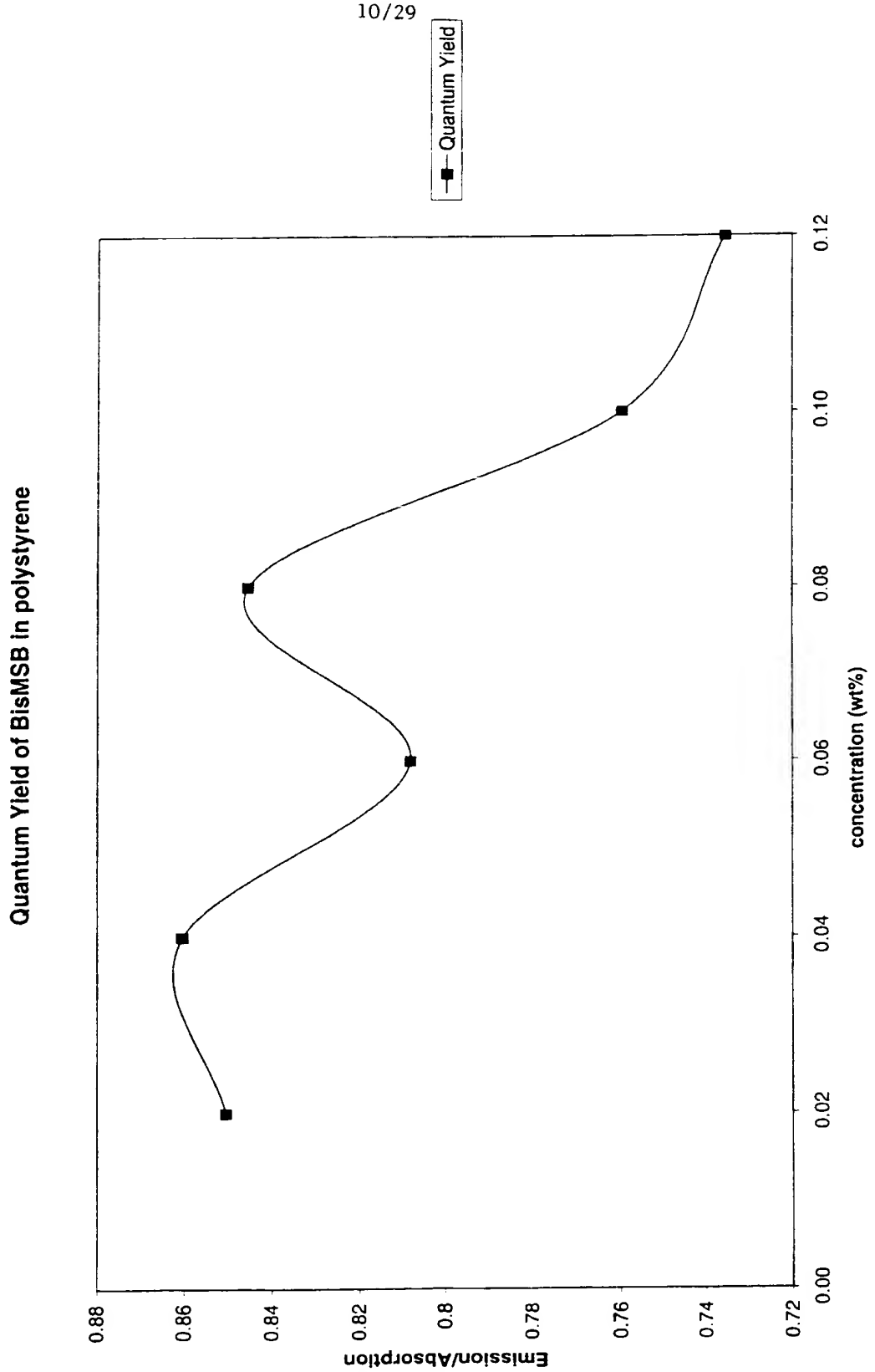
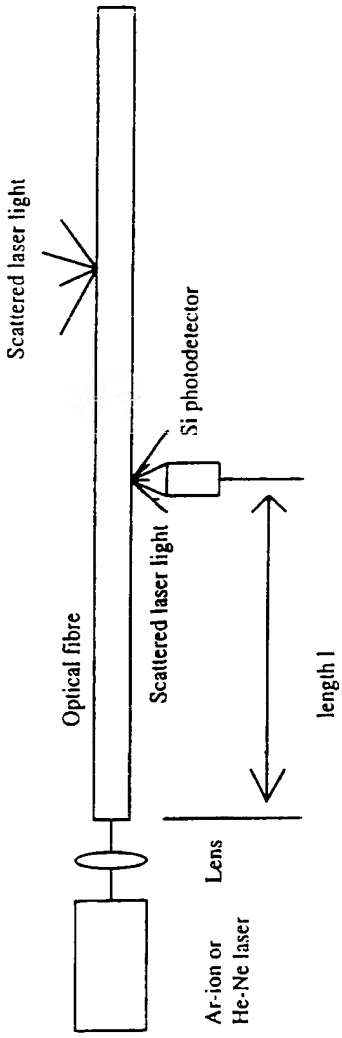

Quantum Yield of BisMSB in polystyrene
Quantum Yield
Emission/Absorption
concentration (wt%)
0.88
0.86
0.84
0.82
0.8
0.78
0.76
0.74
0.72
0.00
0.02
0.04
0.06
0.08
0.10
0.12

Fig 10



Arrangement for light scattering/Absorption measurements

Fig 11

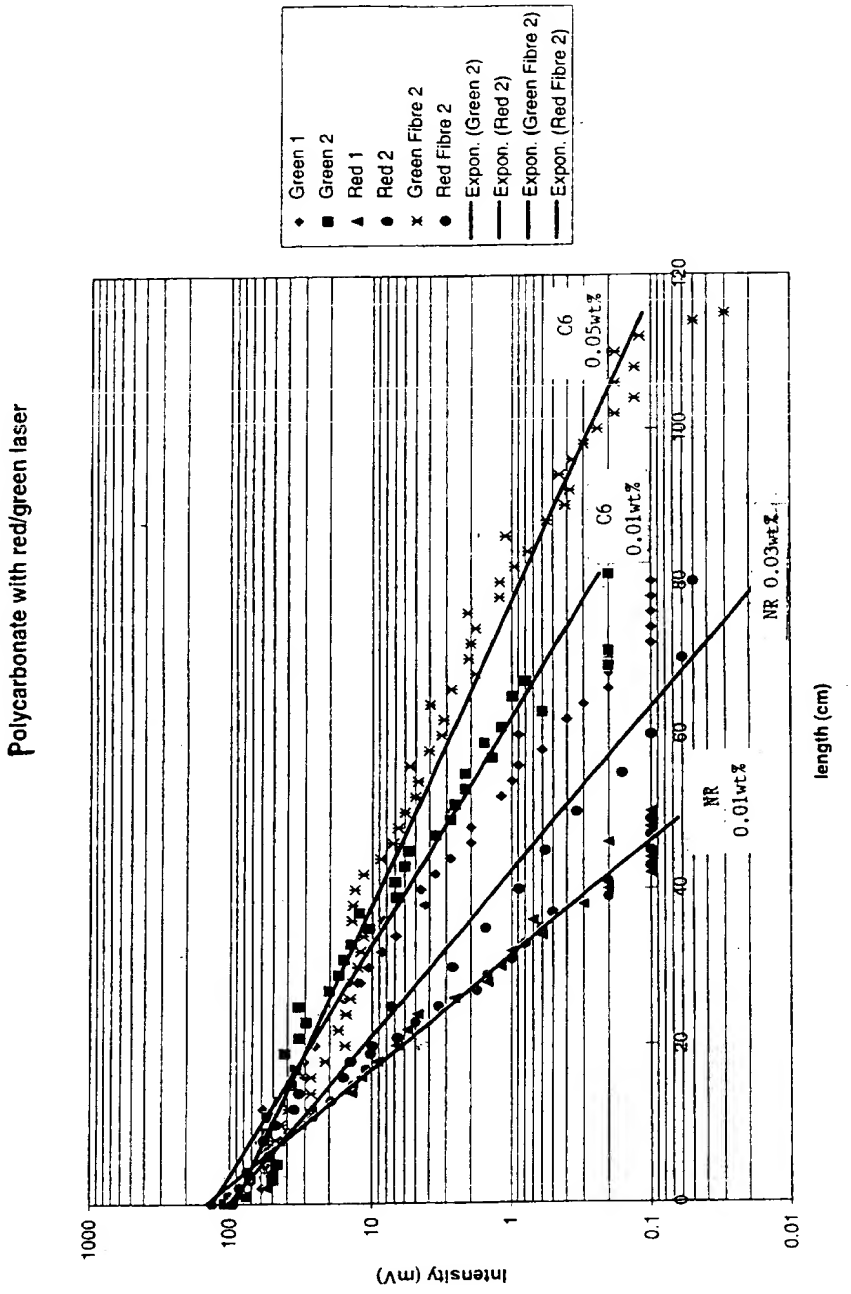

Green 1
Green 2
Red 1
Red 2
Green Fibre 2
Red Fibre 2
Expon. (Green 2)
Expon. (Red 2)
Expon. (Green Fibre 2)
Expon. (Red Fibre 2)
Polycarbonate with red/green laser
Intensity (mV)
1000
100
10
1
0.1
0.01
length (cm)
0
20
40
60
80
100
120
C6 0.05wt%
C6 0.01wt%
NR 0.03wt%
NR 0.01wt%

Figure 12

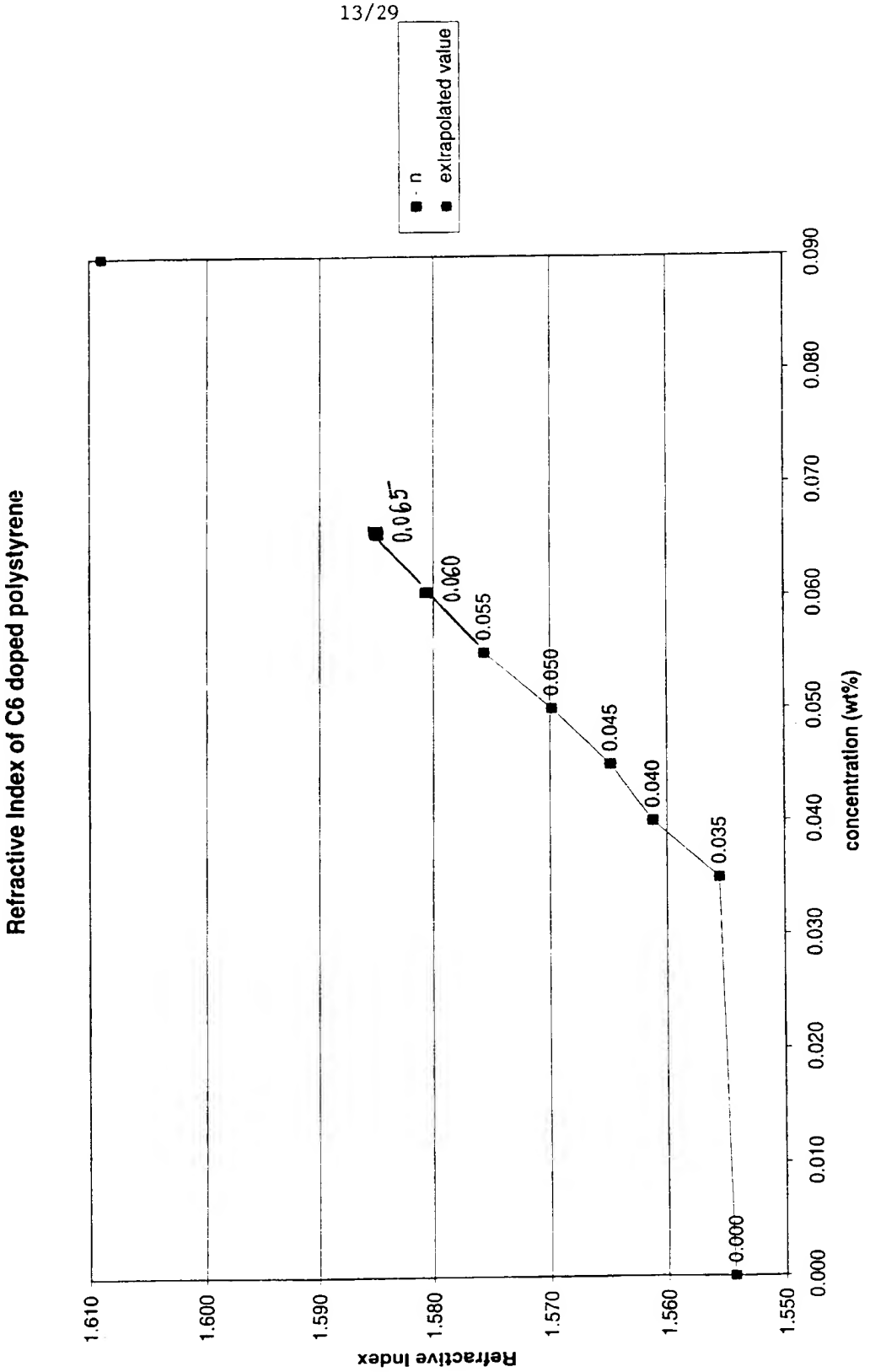

Refractive Index of C6 doped polystyrene
n
extrapolated value
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.000
1.610
1.600
1.590
1.580
1.570
1.560
1.550
Refractive Index
0.000
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080
0.090
concentration (wt%)

Fig 13

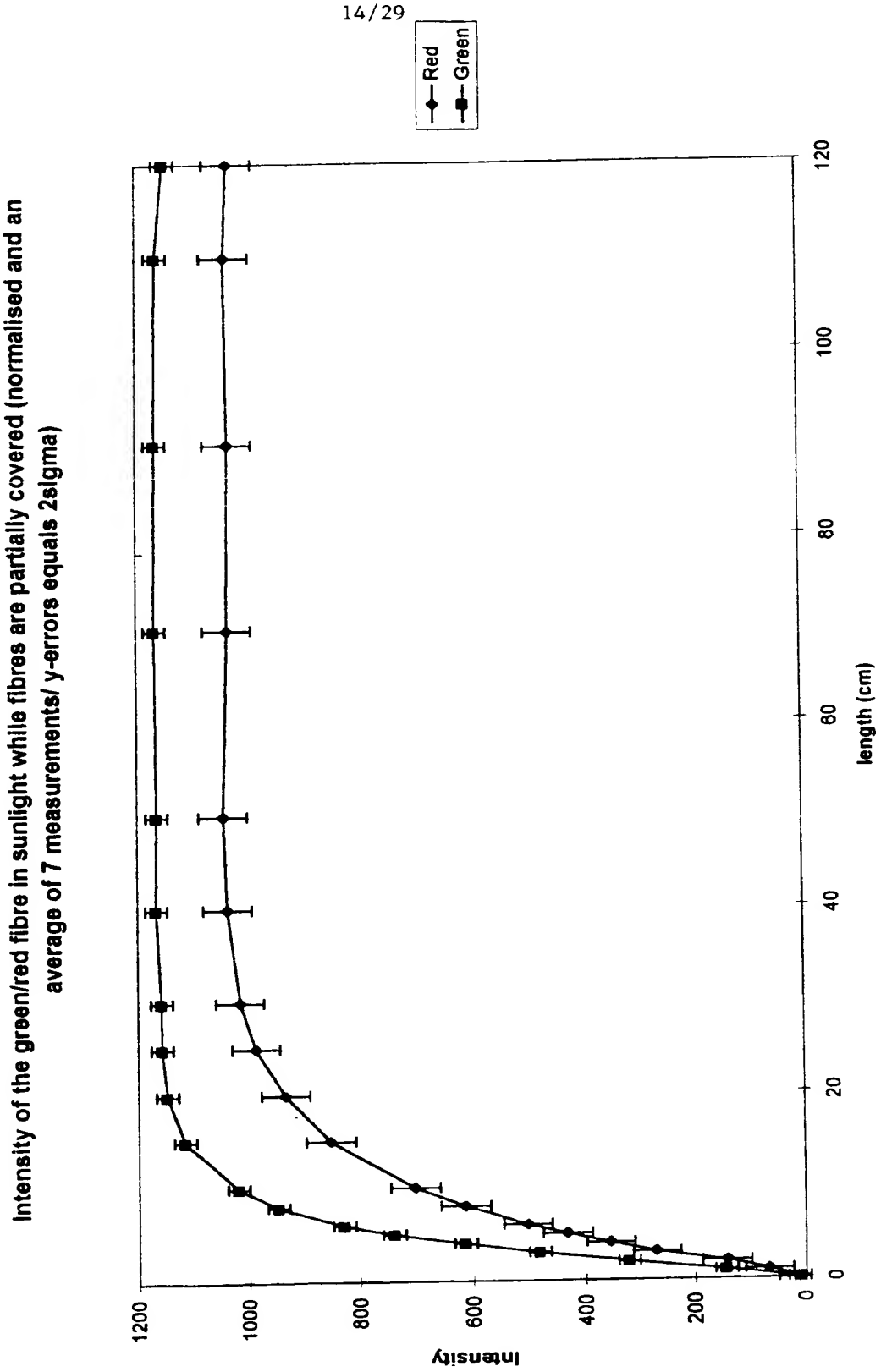

Intensity of the green/red fibre in sunlight while fibres are partially covered (normalised and an average of 7 measurements/ y-errors equals 2sigma)
Red
Green
Intensity
1200
1000
800
600
400
200
0
length (cm)
0
20
40
60
80
100
120

Fig 14

Figure 15

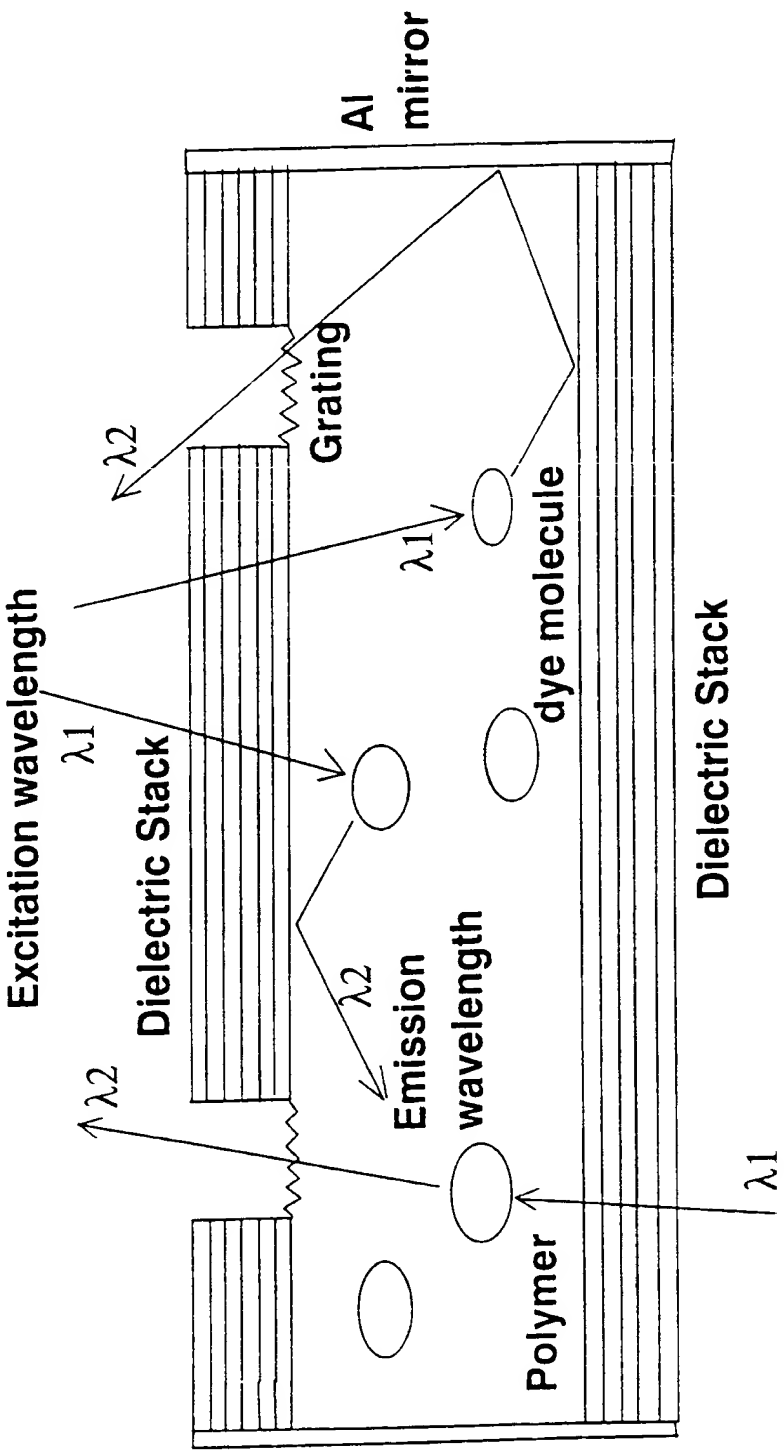
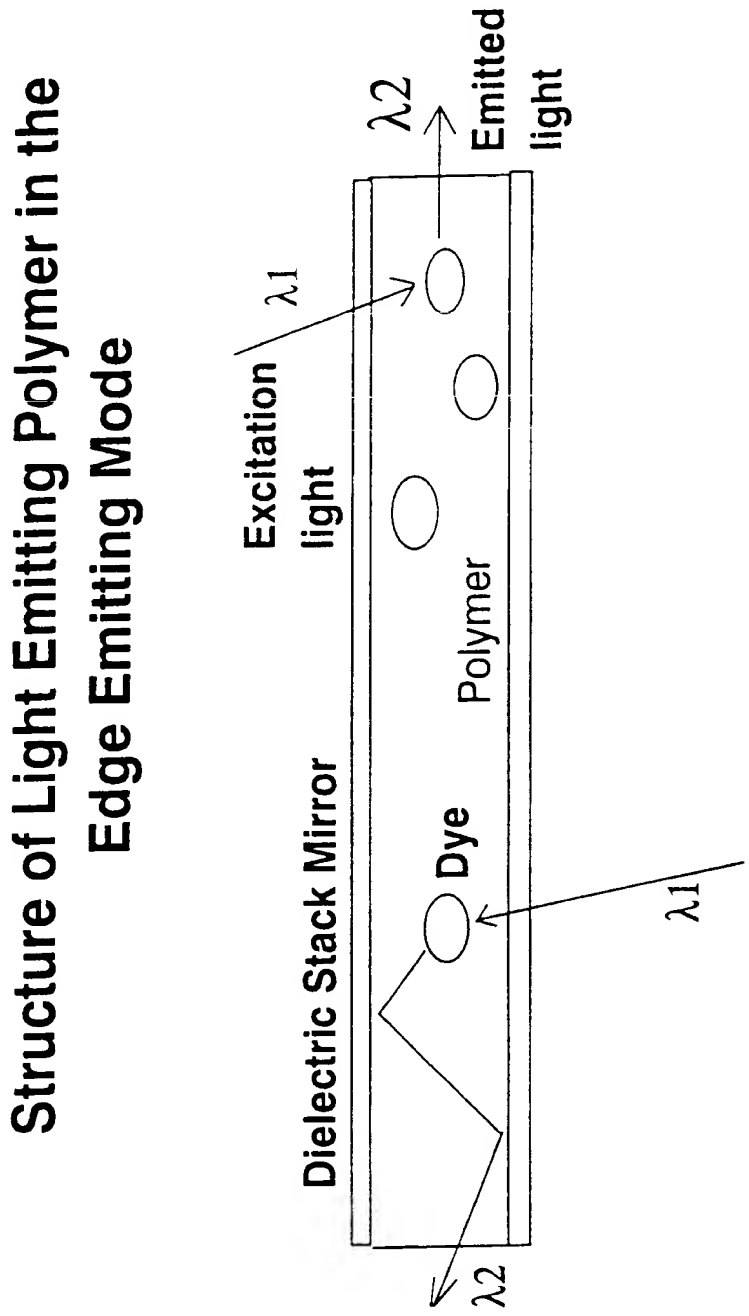

Structure of Light Emitting Polymer
in combined reflective and transmissive mode
Al
mirror
Grating
λ2
λ1
dye molecule
Excitation wavelength
λ1
Dielectric Stack
Dielectric Stack
λ2
Emission
wavelength
λ2
λ1
Polymer

Figure 16


Structure of Light Emitting Polymer in the Edge Emitting Mode
λ2
Emitted light
λ1
Excitation light
Polymer
Dielectric Stack Mirror
Dye
λ1
λ2

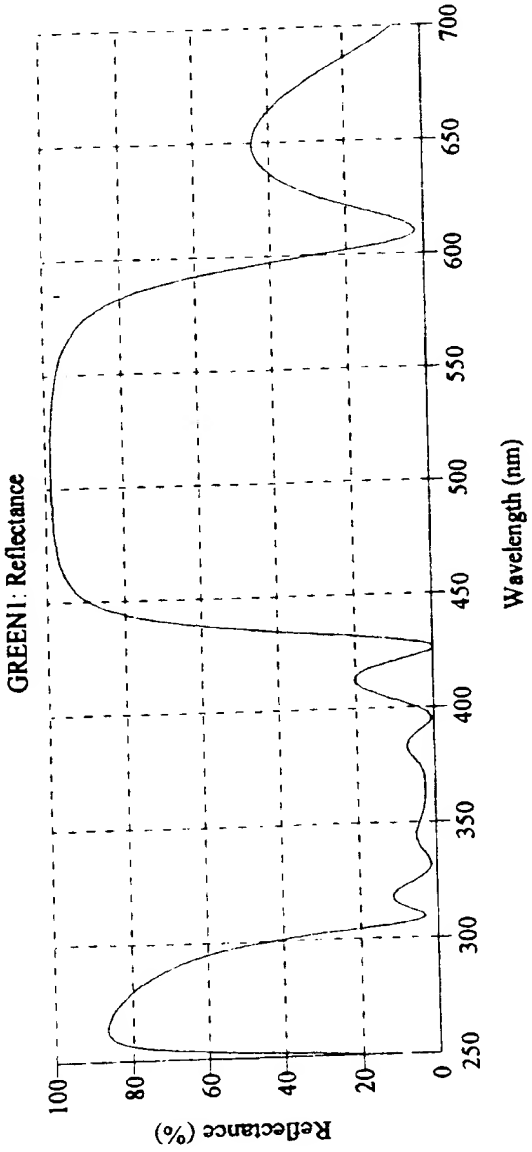

GREEN1: Reflectance
Reflectance (%)
100
80
60
40
20
0
250
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Fig 17

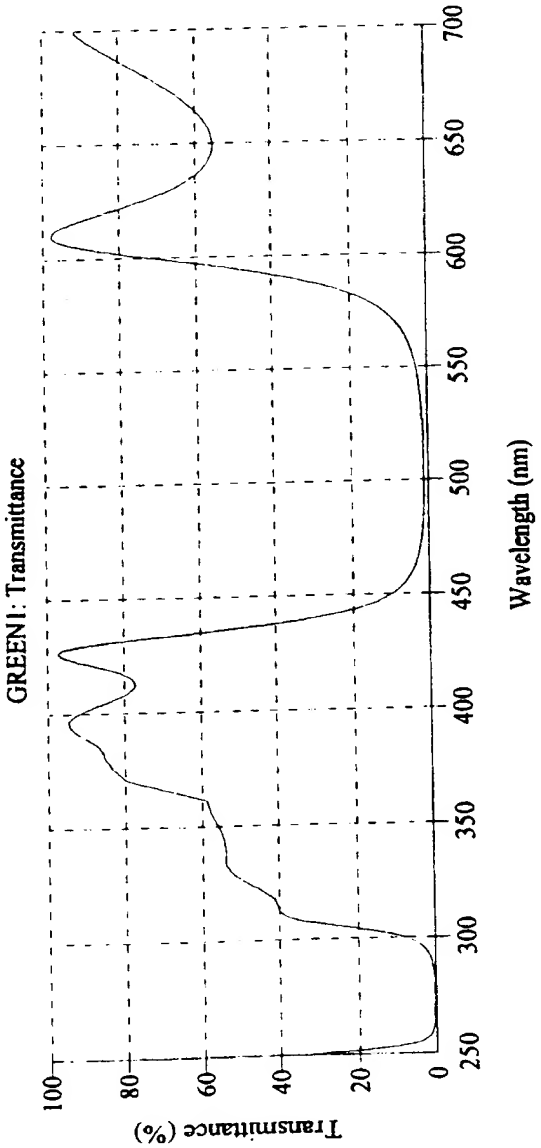

GREEN1: Transmittance
Transmittance (%)
100
80
60
40
20
0
250
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Fig 18

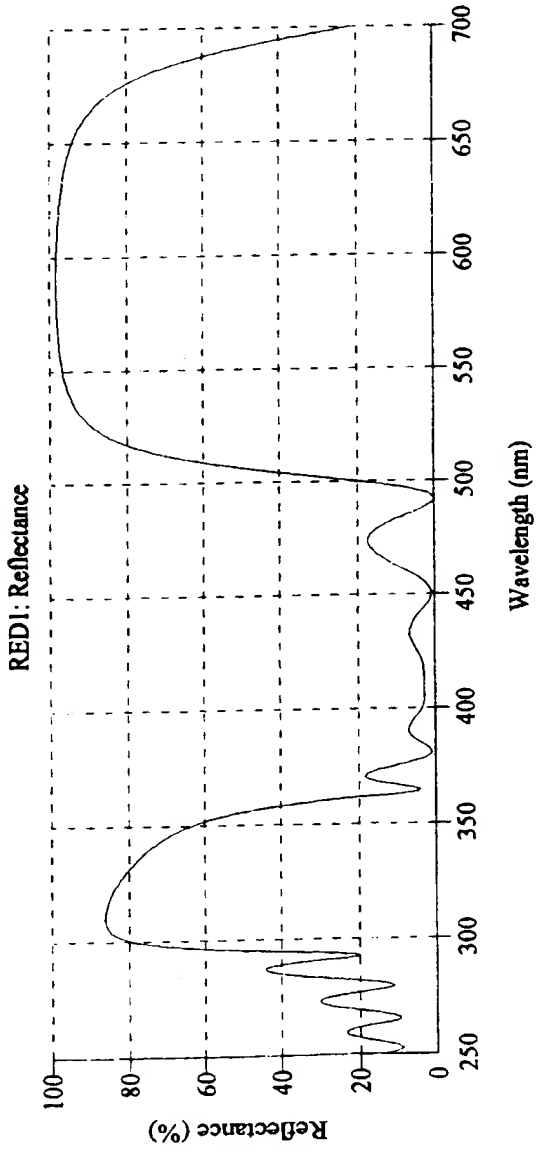

RED1: Reflectance
Wavelength (nm)
Reflectance (%)
100
80
60
40
20
0
250
300
350
400
450
500
550
600
650
700

Fig 19

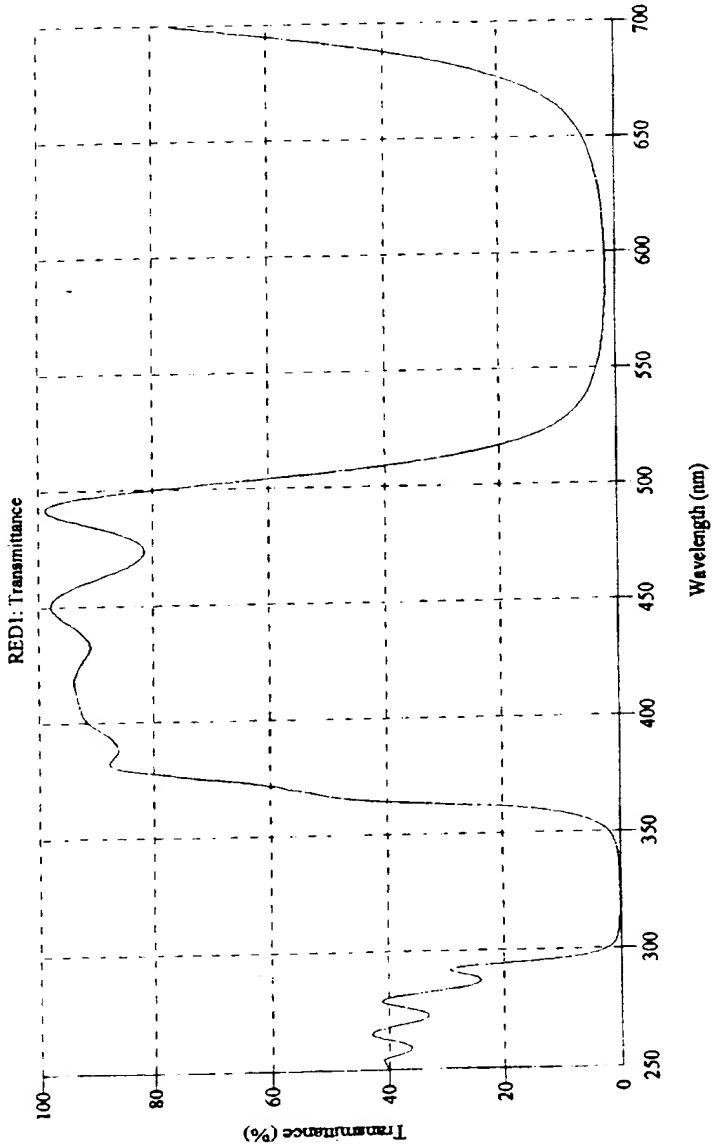
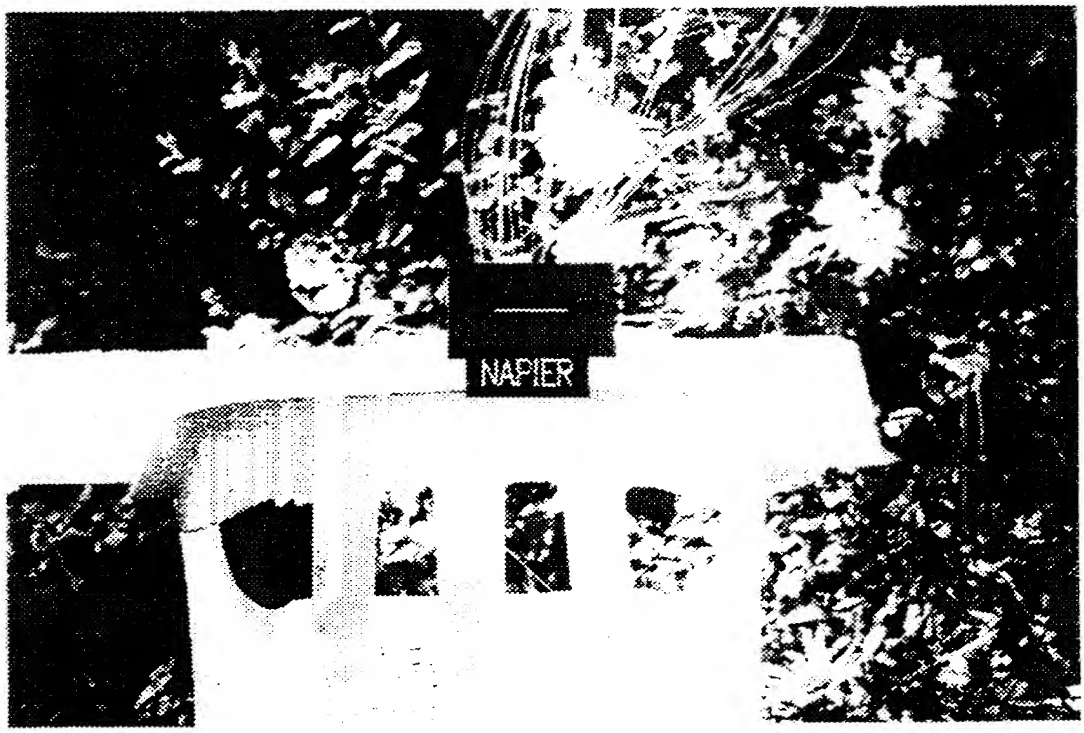
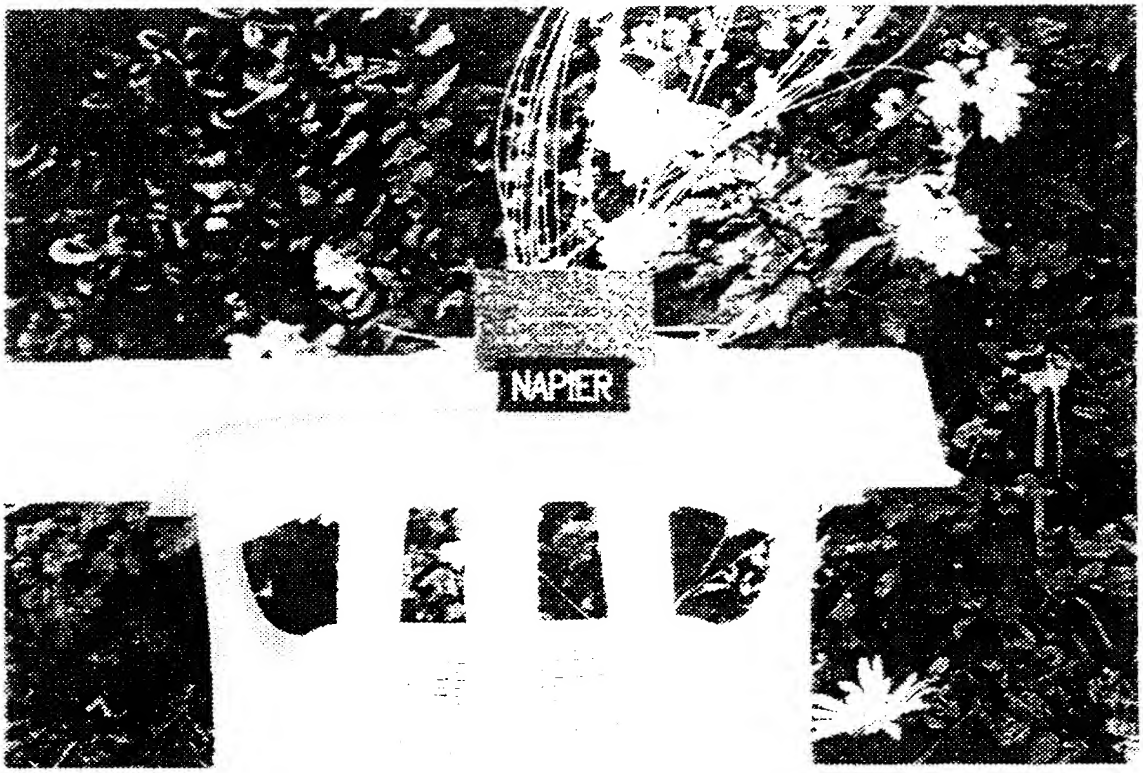

RED1: Transmittance
Transmittance (%)
100
80
60
40
20
0
250
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Fig 20



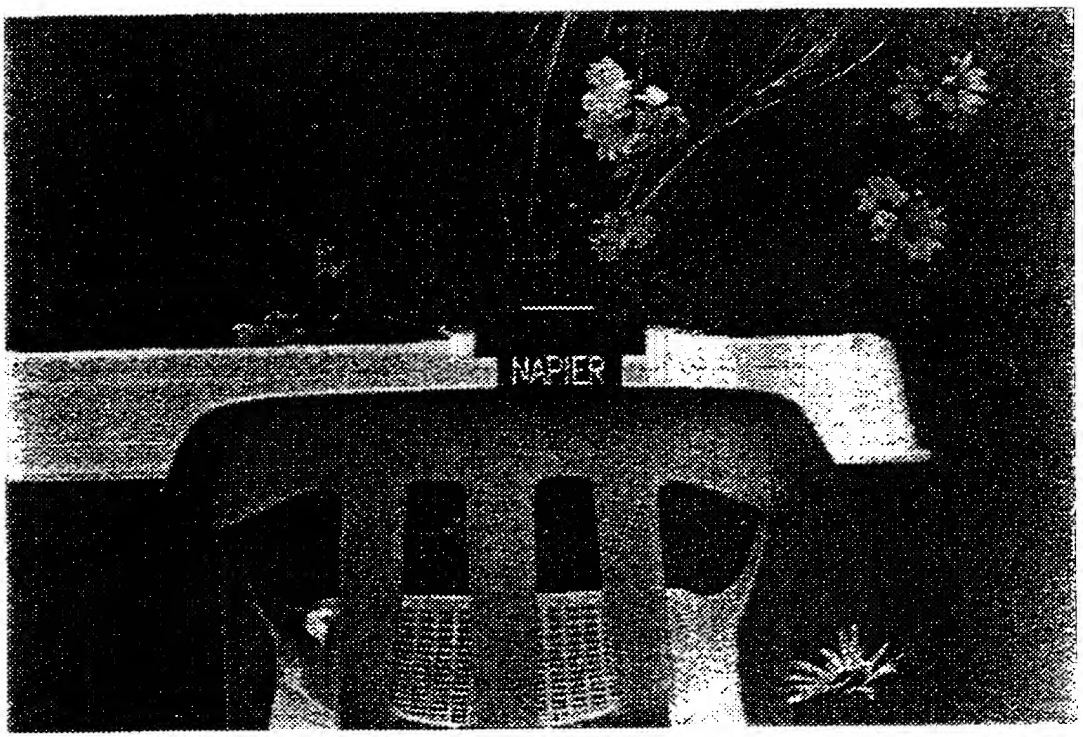
Full Sunlight

Figure 21



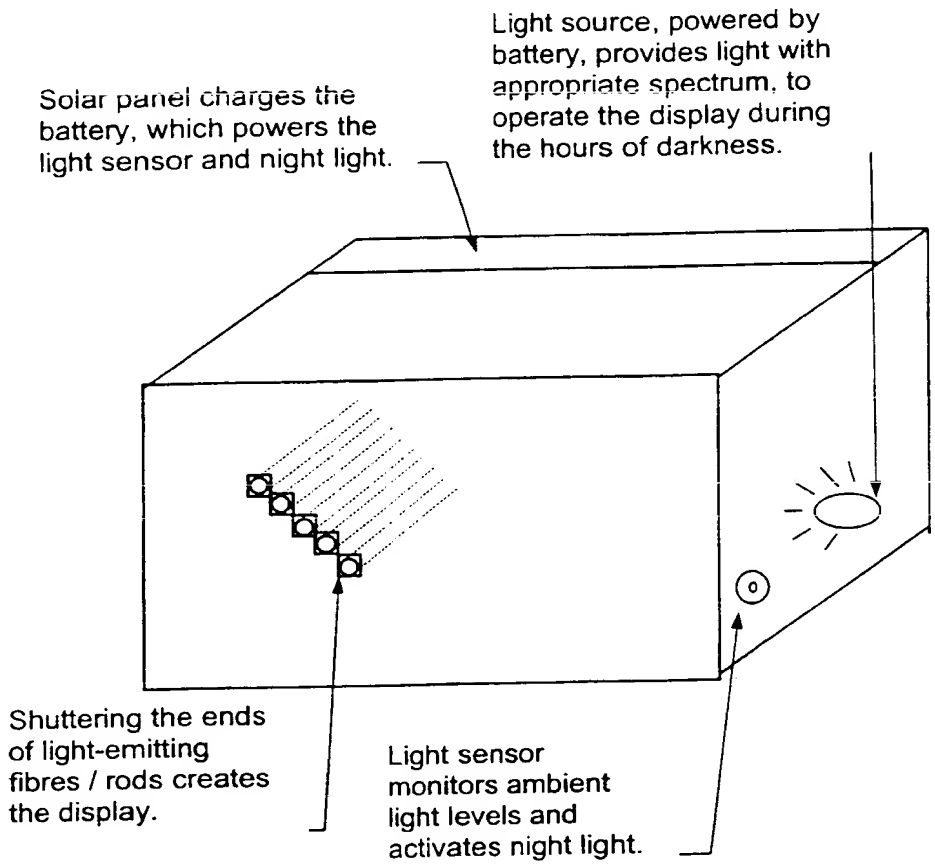
Cloudy

Figure 22



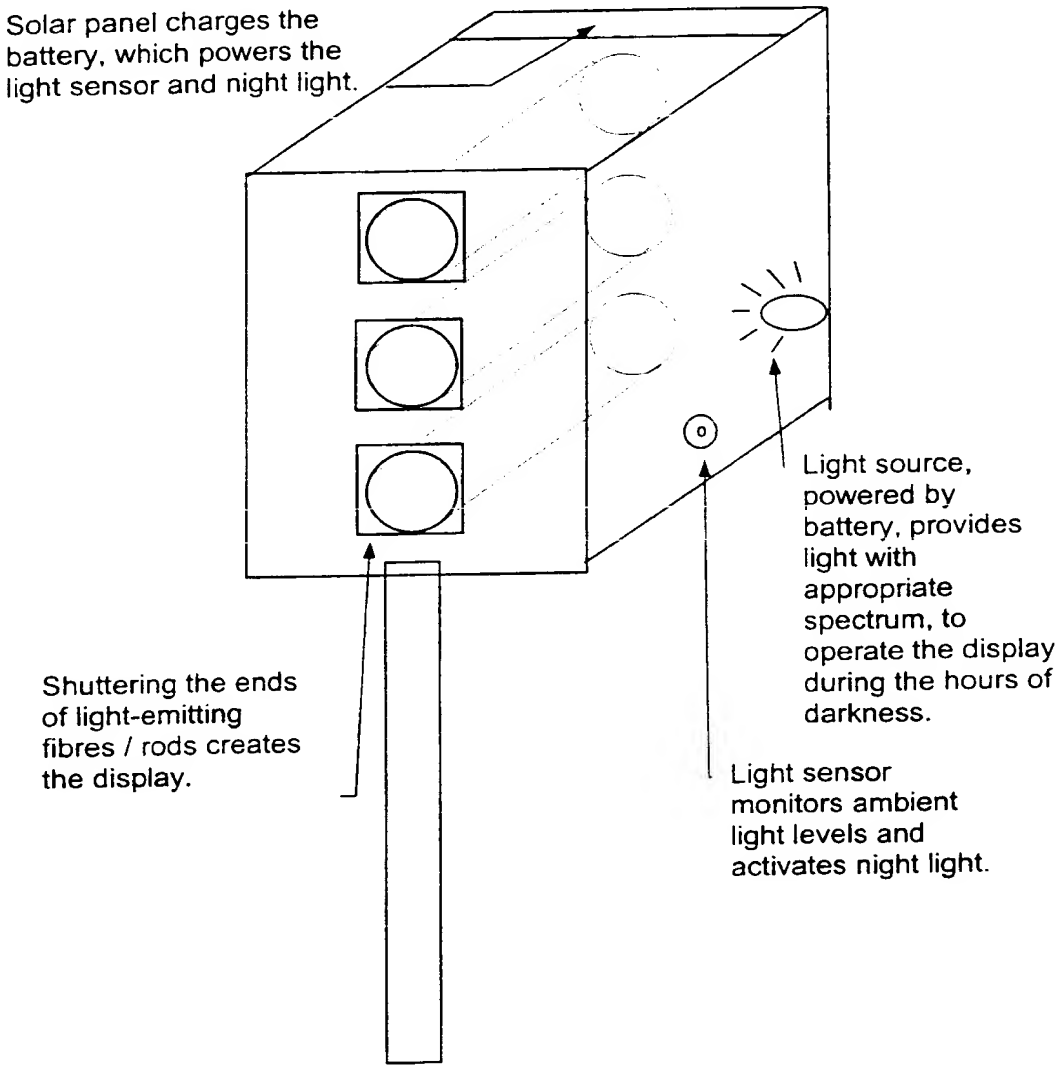
Late Evening
(2 Hours After Sunset)

Fugure 23



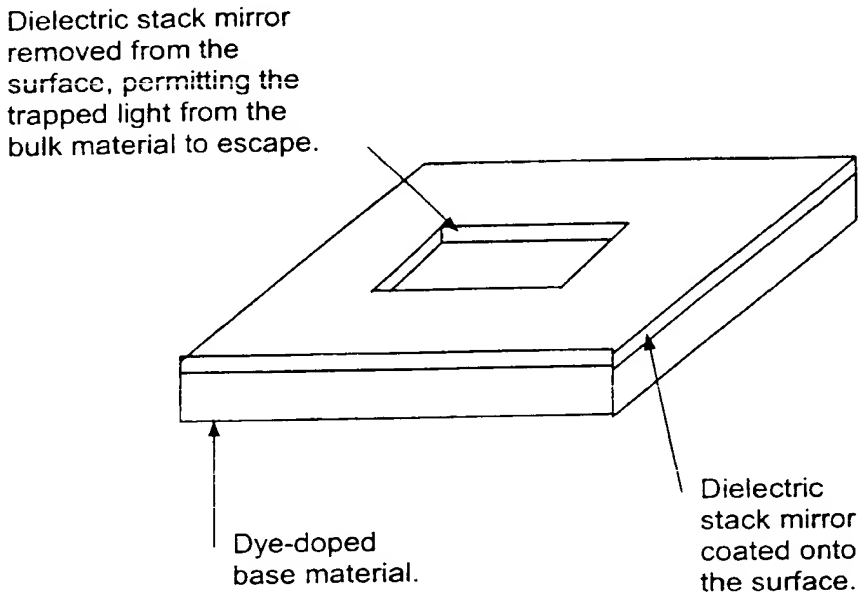
24 Hour Road Signage

Fig 24



24 Hour Traffic Lights

Fig 25



Fixed Advertisement.
Polymer sheet with dielectric stack mirror coated on the surface

Fig 26

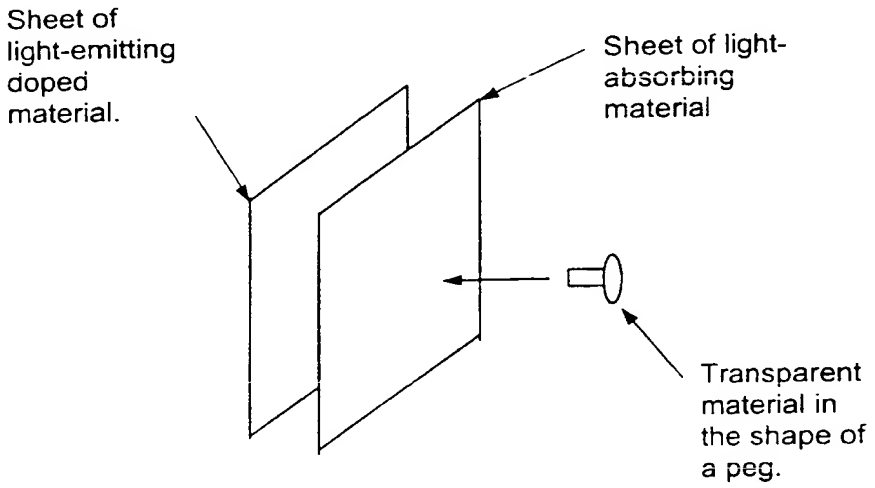

Sheet of light-emitting doped material.
Sheet of light-absorbing material
Transparent material in the shape of a peg.

Fig 27

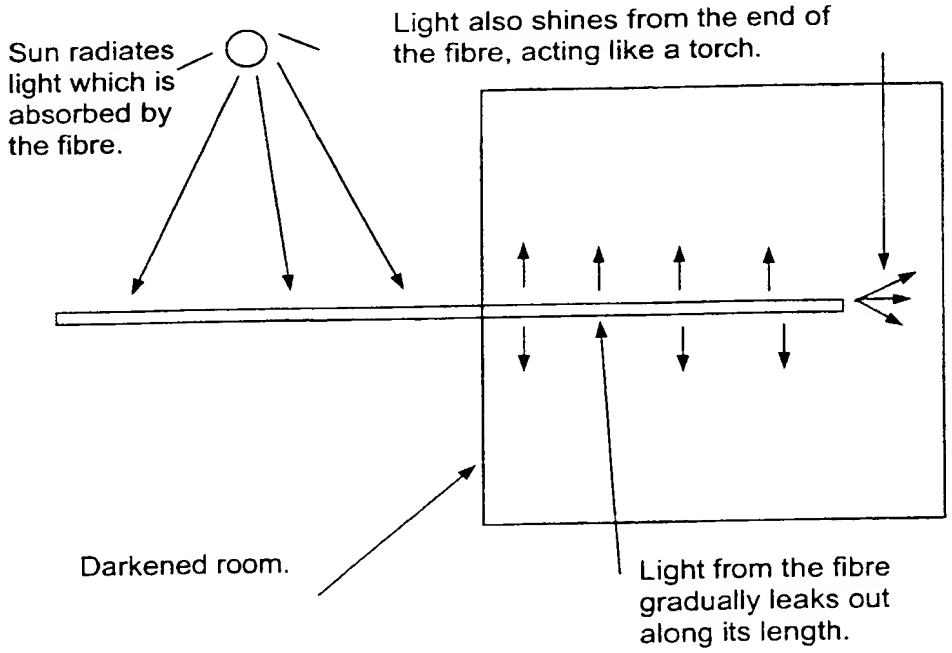

Sun radiates light which is absorbed by the fibre.
Light also shines from the end of the fibre, acting like a torch.
Darkened room.
Light from the fibre gradually leaks out along its length.

Fig 28

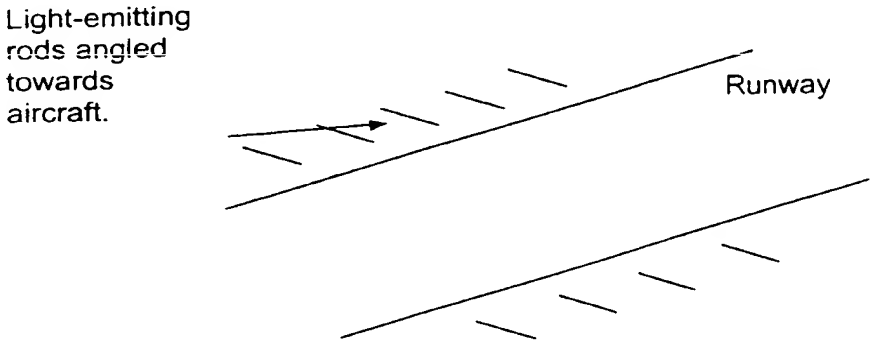
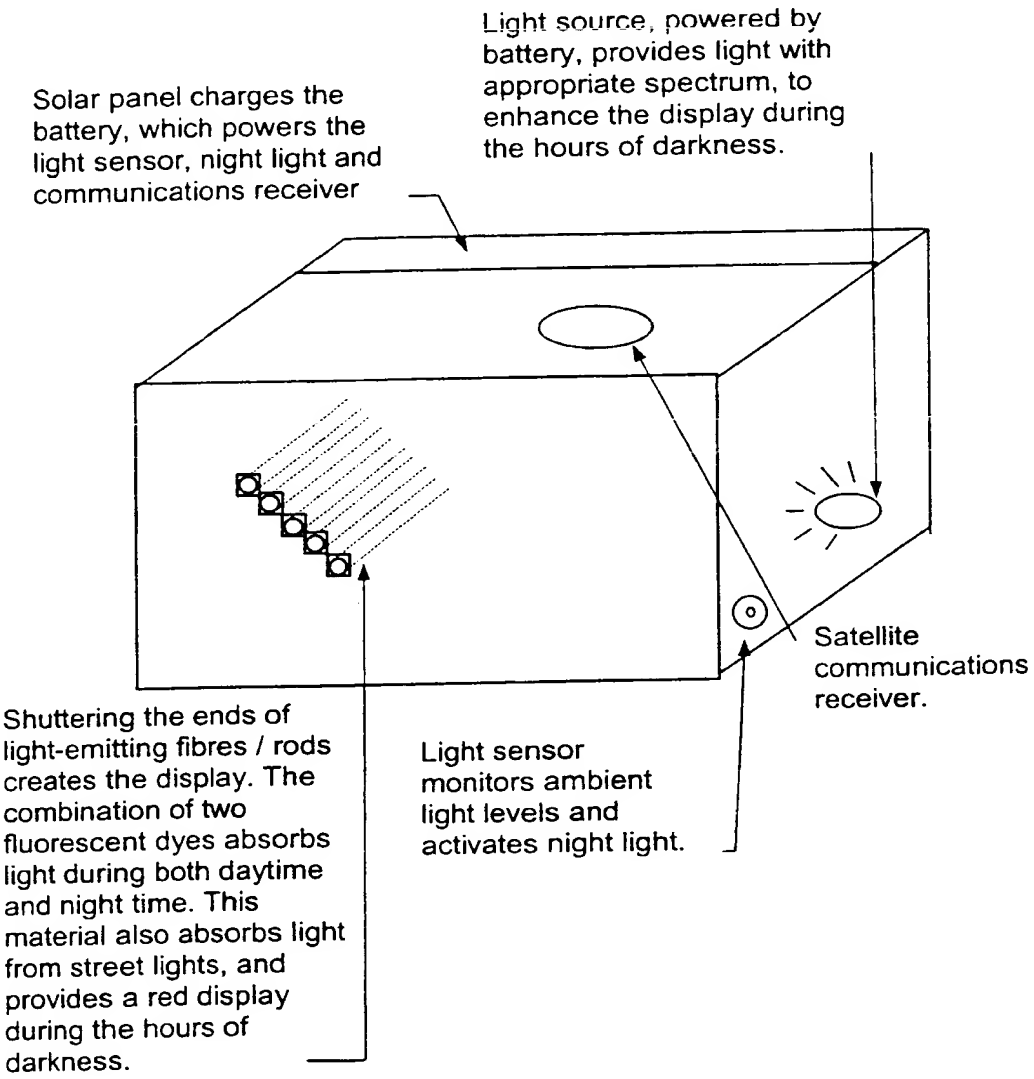


Fig 29



24 Hour Bus Arrival Schedule

Fig 30